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# THE SPECTROSCOPE

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*T. THORNE BAKER*

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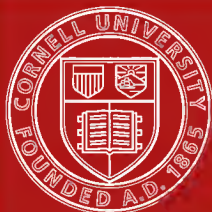
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# Frontispiece.



H

D

DIFFRACTION SPECTRUM OF INCANDESCENT GASLIGHT.

*Fig. 1.*



H

D

PRISMATIC SPECTRUM OF ELECTRIC ARC, SHOWING LITHIUM LINES, &c.

*Fig. 2.*



H

D

PRISMATIC LINE SPECTRUM OF ELECTRIC ARC, SHOWING VANADIUM LINES, AND IMPURITIES SUCH AS CALCIUM, &c., IN THE POLES.

*Fig. 3.*

# THE SPECTROSCOPE

ITS USES IN GENERAL ANALYTICAL  
CHEMISTRY

An Intermediate Text-Book for Practical Chemists

BY

T. THORNE BAKER, F.C.S., F.R.P.S.

AUTHOR OF 'SPÉKTRALPHOTOGRAPHIE, UND DEREN ANWENDUNG,' 'ORTHOCHROMATIC  
PHOTOGRAPHY,' ETC.



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1907

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## P R E F A C E

THE object with which this book has been written is to fill a want which has hitherto been felt by the student of an intermediate text-book which will connect the ordinary treatises on general physics with the modern advanced works on the spectroscope. Present-day apparatus, moderate in cost, has been described as fully as possible, in order to assist the reader in the choice of any instruments he may want, and the applications of spectroscopy to chemical analysis have been given the chief consideration. Special attention has been directed to the photographic side of the subject, and the construction of simple and economical apparatus described. References have been made to modern work with a view to pointing out in what directions the openings for research work lie. The astronomical side of the subject has been left entirely untouched. To those acquainted with elementary physics the book will, it is hoped, provide sufficient information to enable them to negotiate without difficulty the advanced treatises on the subject, to which are left the subject of the echelon grating.

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#### ERRATA.

Page 5, line 21, for 'H (violet) Wave-length 3967' read 'H (violet) Wave-length 3969.'

Page 82, line 21, for 'Yerks' read 'Yerkes.'

Page 126, the second half-tone block is the wrong way round—i.e., the left side should be the right.

Page 53, line 32, for 'absorbtive', read 'absorptive'.



# THE SPECTROSCOPE

## CHAPTER I

Colour — Refraction and dispersion — Absorption — The spectrum, prismatic and diffraction—Nature of spectra—Principles of the spectroscope.

WHITE light, as 'daylight' and most ordinary sources of artificial light are called, is in reality a composition. A beam of white light can be split up into a number of beams of coloured light, and these, if recombined, would once again produce the sensation of white light. Light is caused by electro-magnetic vibrations of the ether, which travel in the form of waves, meet the eye, and stimulate the optic nerves. According to the Young-Helmholtz theory of colour, three *primary colour* sensations exist, and the eye possesses three sets of nerves, which, when excited, give the sensations of red, green, and violet respectively. The sensation of white can be produced either when rays of light of three selected frequencies enter the eye, or when rays of a very great number of frequencies, to be considered later, enter the eye. The sensations of various colours are produced by the three sets of nerves being stimulated, singly or together, to different degrees.

If we see an incandescent gas light side by side with an ordinary fish-tail burner, we are at once struck with the contrast in colour between the two. The incandescent gas

light appears distinctly whiter with a tinge of green; the fish-tail burner gives a very 'yellow' light. The two illuminations are composed of widely different proportions of coloured components. Some method of qualitatively analysing any kind of 'light' will reveal that which the eye is incapable of doing, and we require for such purpose some means of separating up light into its various constituents.

If a ray of white light,  $AB$ , fall obliquely upon a parallel-sided piece of glass,  $MN$ , on entering the glass it is bent out of its course, or refracted, and travels along some such path as  $BC$ . Light travels with different velocities in air and

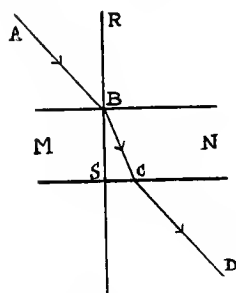


FIG. 1.

glass. On emerging it assumes its original direction, and travels along  $CD$  with the same velocity it had before entering the glass. If  $RBS$  be drawn normal to the glass, the angle  $ABR$  is called the angle of incidence, and the angle  $SBC$  the angle of *refraction*.  $AB$ ,  $RB$ , and  $BC$  all lie in one plane, and sine  $ABR$  bears a constant ratio to sine

$SBC$ , the ratio  $\frac{\sin ABR}{\sin SBC}$  being called the *refractive index* of the medium (in this case glass) relative to air, and being hereinafter denoted by the letter  $\mu$ . If  $ABR = 0$ , or  $AB$  is normal to  $MN$ ,  $SBC$  is also necessarily  $= 0$ ; or, in other words,  $BC$  is also normal, and coincident with  $BS$ .

Let us now suppose the direction of the ray to be reversed, and  $CB$  to emerge from the glass to air, air being a *less dense medium* than glass. When  $CB$  makes a sufficiently large angle with  $BS$ ,  $BA$  will make a right angle with  $BR$ . As soon, then, as  $CB$  makes a slightly larger angle still,  $a$ , with  $BS$ ,  $BA$  will clearly lie inside  $MN$ ; it will, in fact, be *totally reflected* within the medium, making an angle also  $= a$  with  $BS$ .



The ratio  $\frac{\sin \text{SBC}}{\sin \text{RBA}}$  now becomes  $\sin \text{SBC}$ ,

as  $\text{RBA}$  equals  $90^\circ$ , and  $\sin 90^\circ = 1$ .

$$\therefore \sin \text{SBC} = \frac{1}{\mu},$$

from which  $a$  is easily calculated.  $a$  is termed the *critical angle* for the particular medium.

Now let us examine the case where  $\text{MN}$  is not parallel-sided, but where the two sides make an angle with one another, which we will call  $\beta$ . Here  $\text{AB}$  meets the surface  $\text{MN}$  at  $\text{B}$ , and  $\text{BX}$  is drawn normal to  $\text{MB}$ .  $\text{BC}$  is the refracted ray, and  $\frac{\sin \text{ABX}}{\sin \text{CBY}} = \mu$ .

There is one position possible such that  $\text{BC}$  will form an isosceles triangle  $\text{MBC}$ , when also  $\text{CD}$ , which is the *emergent ray*, will form an angle  $\text{DCM} = \text{ABM}$ .

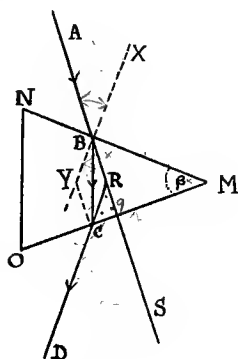


FIG. 2.

If  $\text{CY}$  be drawn perpendicular to  $\text{MC}$ , the angles  $\text{MBY}$ ,  $\text{MCY}$ , are both right angles; hence  $\text{BYC}$ ,  $\text{BMC}$ , equal two right angles. Also  $\text{BYC}$ ,  $\text{YBC}$ , and  $\text{YCB}$  equal two right angles; hence  $\text{BMC}$  equals  $\text{YBC} + \text{YCB}$ , or the angle  $\text{YBC} = \frac{1}{2}\beta$ . Also  $\text{CRS}$  equals  $\text{CBR}$  and  $\text{BCR}$ , or  $\text{CBR} = \frac{1}{2}\text{CRS}$ .

Now,  $\text{ABX}$  equals  $\text{YBC}$  plus  $\text{RBC}$ , or angle  $\text{ABX} = \frac{1}{2}\beta + \frac{1}{2}\text{CRS}$ .

As  $\text{ABX}$  is the angle of incidence, call it  $i$ , and let  $\text{CRS}$  be called  $d$ , the angle of deviation;

$$\text{then } i = \frac{1}{2}\beta + \frac{1}{2}d,$$

$$\therefore \sin i = \sin \frac{\beta + d}{2};$$

$$\text{and } \frac{\sin i}{\sin YBC} = \frac{\sin \frac{\beta+d}{2}}{\sin \frac{\beta}{2}},$$

$$\therefore \mu = \frac{\sin \frac{\beta+d}{2}}{\sin \frac{\beta}{2}}.$$

Suppose that now MNO be a glass prism, or wedged-shaped piece of glass, and AB represent a ray of light. It will emerge from the prism along the path CD. But if AB be a ray of white light, we shall get a ray of one colour only along BC, CD. White light is composed of violet, blue, green, yellow, orange, and red constituents, and each constituent will be *deviated to a different extent*. Instead, therefore, of a single ray, BC, we should have a number of such rays, each of a different colour, and each making a slightly different angle with the normal BY. As these rays leave the prism they become still more dispersed, and hence an eye placed at D would see a band of colours, the red the least deviated, the yellow and orange more deviated, the blue and violet most deviated. This band is called the *visible spectrum*.

If now a pure yellow ray only be represented by AB, of course a pure yellow ray only will emerge along CD, and if MBC form an isosceles triangle, CBY will be the minimum deviation possible from the original path. The prism is then said to be in the position of *minimum deviation* for the particular circumstances. By measuring the angles ABM, DCM, and  $\beta$ , we could find the refractive index,  $\mu$ , for the substance of which the prism is composed.

If a ray of white light, AB, cause a spectrum FGH, F being the red end, H the violet, then the angle between the limbs of the band FGH is dependent on the dispersive power of the prism used. The greater the dispersive power

the greater the angle between FC and HE. The *dispersive power of prisms* will be considered more fully later on.

Light waves are extremely short, and the wave-length of violet light of a particular kind is  $4000 \times 10^{-8}$  centimetres. The wave length of light of a certain green kind is  $5000 \times 10^{-8}$  centimetres, that of light of a certain orange kind

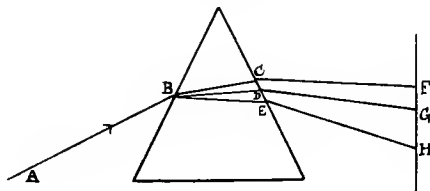


FIG. 3.

$6000 \times 10^{-8}$  centimetres. It might, therefore, be thought that the angle between FC and GD, if these be supposed to be the orange and green rays in question, would be the same as the angle between GD and HE, if these represented the green and violet rays in question. This, however, is by no means the case. With all prisms the yellow, orange, and red

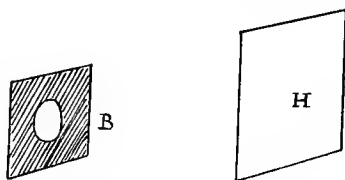


FIG. 4.

portions of the spectrum are cramped together; the blue-violet portion is quite disproportionately long; the dispersion of prisms is therefore said to be abnormal. We shall now, however, proceed to study the production of a spectrum in which the distribution of colour is proportional to its wave-length.

It will first be necessary to show that light does not neces-

sarily travel in a uniformly straight line. If a parallel beam of light fall on a screen H, and at some distance from it an opaque screen B be placed, with a central hole in it, each portion of the hole becomes a source of illumination, and disturbances go forth from every point in the hole. In the next figure, let P be a point on the screen, and let CD represent the hole in the opaque screen.

With P as centre, describe a number of spheres, with radii equal to PA,  $PA + \lambda/2$ ,  $PA + 2\lambda/2$ ,  $PA + 3\lambda/2$ , and so on, where  $\lambda$  is one wave-length of monochromatic light. Consider the ring between two consecutive radii, B and C, where, if BR

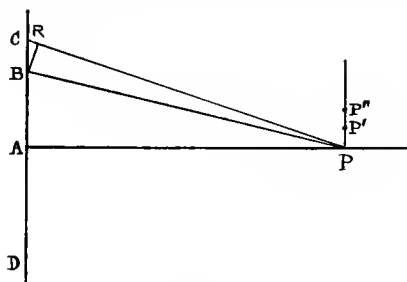


FIG. 5.

be drawn perpendicular to PC, CR will equal  $\lambda/2$ . Let the mean of AB and AC =  $m$ , and the distance of BC from P =  $d$ , then the area of the ring will be  $2\pi m \cdot BC$ , or, by similar triangles,  $2\pi \lambda/2 \cdot d = \pi \lambda d$ ;

$$\therefore \frac{\text{the area of a ring}}{\text{its distance from P}} = \lambda \pi = \text{constant.}$$

Next consider DC as made up of a number of these rings, which are obviously of equal illuminating power. There is a condensation and retardation in each complete wave; any one of these half-wave-length rings therefore neutralizes another immediately next it. The total effect at P is due simply to the disturbance immediately surrounding the point A.

Now suppose an opaque object AD be placed in front of half the hole, the amplitude of the disturbance at P becomes halved. If AD be lowered a distance  $\phi$ , equal to the width of the first half-wave-length ring, the effect at P will be brighter, as the waves in this disturbance are, of course, in the same phase as those in the upper half of the ring. If we remove AD still lower by the width of another ring, the effect from this neutralizes the one above it, the waves being in opposite phase, and the effect at P is less, and so on.

By converse reasoning, if AD be covered once again, P could be moved to a position P', where  $AP' - AP = \lambda/2$ , and to another P'', where  $AP'' - AP' = 2\lambda/2$ , and so on, so that a series of bright and dark points would alternately result. Hence

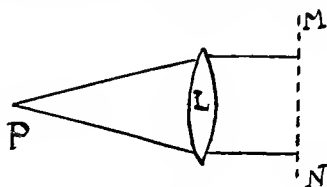


FIG. 6.

on a screen placed at P there would be a series of bright and dark points, or maxima and minima of illumination. These are due to the diffraction of light at the edge of the opaque object AC.

On this property of diffraction depends the *grating*, one of the most satisfactory instruments for forming a spectrum. Let rays of light from a source P meet a lens L (Fig. 6), so that each wave leaves L in the same phase and a parallel beam of light falls normally upon the grating MN.

Let the grating in this case consist of a piece of plane glass ruled with a number of equidistant black lines, so that AB, CD, etc., become light sources, and we may regard each luminous ether particle therein as a fresh disturbance; BC, DE, etc., remain dark. Consider a point S. If a wave of

light reaches S from A, and another from C, AR is the difference in path travelled by the two, CR being drawn perpendicular to AS. If AR be equal to an even number of half wave-lengths, the waves from A and C will arrive at S in the same phase, and give a bright image. If AR be equal to an odd number of half wave-lengths, the waves from A and C will arrive at S in opposite phase and neutralize one another; hence a dark image—*i.e.*, no image—will be formed. Now AR obviously varies with light of different wave-lengths, to satisfy either of these conditions—*i.e.*,  $\lambda$  varies between about  $3500 \times 10^{-8}$  centimetres and  $7500 \times 10^{-8}$  centimetres for the visible spectrum. A series of continuous positions can

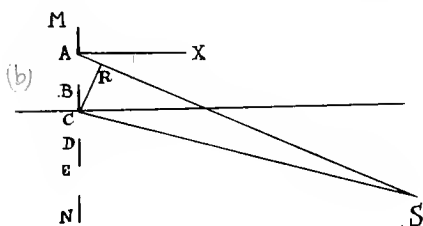


FIG. 7.

be found for S for light of each wave-length, and consequently we get a spectrum in which the angular deviation of any coloured ray is proportional to its wave-length.

It will be seen from Fig. 7 that

$$\frac{AR}{AC} = \cos CAR, \text{ or } \sin RAX;$$

$\therefore \frac{AR}{AC}$  = the sine of the angle of deviation of the ray from the normal AX. Now if we denote the ruling width AC by the letter  $b$ , we get the relation

$$\lambda = b \sin RCA,$$

or, calling the angle of deviation  $\theta$ ,

$$\lambda = b \sin \theta.$$

It is quite evident that if AR be equal to two whole wave-

lengths, or three (and so on), a bright image could be obtained at some such position as S. The general expression thus becomes

$$n\lambda = b \sin \theta_n,$$

where  $n$  is an integer 1, 2, 3, etc., and  $\theta_n$  the angle of deviation when  $n$  is one of these numbers. Where  $n=2$ , we should speak of the spectrum produced as being of the second *order*, and so on.

Where the grating is inclined at an angle to the plane of the collimating lens it can be readily shown that, if  $\phi$  be this angle,

$$n\lambda = b (\sin \phi + \sin \theta_n).$$

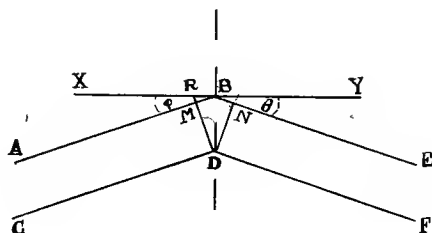


FIG. 8.

For, if in Fig. 8 AB, CD be two rays, portions of which are diffracted along BE, DF respectively, and DM, DN be drawn perpendicular, then MB + BN is the difference in the march between the diffracted rays BE and DF. Let XBY be a line drawn normal to the grating, then the triangles MRB and MDB are similar, so that the angle MDB =  $\phi$ , and MB = BD sin  $\phi$ ; but BD =  $b$ ,  $\therefore$  MB =  $b \sin \phi$ . Also BN =  $b \sin \theta$ ; hence we get the relation that

$$\lambda = b \sin \phi + b \sin \theta,$$

or, generally—

$$n\lambda = b (\sin \phi + \sin \theta_n),$$

for wave-length determination.

It will thus be readily seen that, when a spectrum is produced by throwing collimated light upon a ruled polished

surface, a change of sign is introduced, so that for a reflection grating we have  $n\lambda = b(\sin \phi - \sin \theta_n)$ .

In practice, between 10,000 and 20,000 lines to the inch are usually ruled on a plane grating; hence, if the beam of parallel light cast upon it be 4 square centimetres in area, some thousands of parallel diffracted rays of each colour leave the grating in the same phase. By means of an objective lens these rays are concentrated, and produce a bright line, as the action of the lens is to combine all parallel rays at the focus, the waves being in the same phase when they arrive at the focus.

We are now in a position to understand the principles of the spectroscope, which is merely an instrument used to

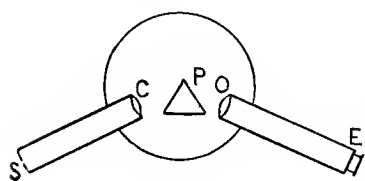


FIG. 9.

split up a beam of light into its constituent colours. In its simplest form a spectroscope is constructed as shown in Fig. 9. Here SC is a brass tube, with a narrow slit at S, vertical to the plane of the paper. C

is a lens of focal length SC, so that all light from S emerges from C parallel to the axis. P is a prism, arranged so that the light from C falls upon one face in the angle of minimum deviation. OE is a telescope, the dispersed beam of light emergent from P being brought to a sharp focus by the lens O, which is usually of the same focal length as C. At E is an eye-piece which enlarges the image formed by O. The telescope OE is capable of rotation about an axis whose centre is at P, and the angle which OE makes with SC is read off on a divided circle by means of a vernier. The eye-piece E is provided with crossed spider-webs, so that any particular ray can be brought into view in the centre of the field; the position of the telescope is then ascertained by means of



## SPECTROSCOPE ESSENTIALS

the vernier, and the angular deviation for that ray, obtained. The various movements and arrangements of parts in a spectroscope will be fully considered in the next chapter, when many of the principal modern forms of instruments will be described. We shall, therefore, conclude this chapter by briefly describing the plan on which the plane grating spectroscope is constructed.

Here we again have a slit *S* and a collimating lens *C*, so arranged that all rays emerge from *C* parallel and in the same phase. The collimator is fixed to the divided circle, whilst the telescope is capable of rotation; in the centre of the circle the grating *G* is placed, so that the lines ruled on it are parallel with the slit *S*; the grating may be fixed either normally to the optic axis of the collimator, so that the rays from *C* meet it normally, or at some angle; as when normal the wave-length of any ray is determined by the simple formula

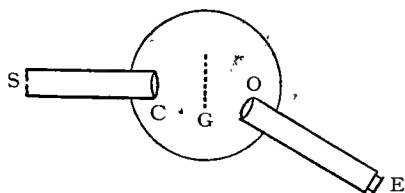


FIG. 10.

length of any ray is determined by the simple formula

$$n\lambda = b \sin \theta_m,$$

it is most convenient to use it in this position. If there are *n* rulings on the grating, which is *m* centimetres diameter,

*b* will be equal to  $\frac{n}{m}$ ; *n* parallel diffracted rays of each colour

will leave the grating, and by means of the objective lens *O* these are brought to a focus; hence by means of the eye-piece *E* we should see a bright yellow line at one angle, a green line at a slightly less angle, a blue line at a still less angle, and so on. These bright lines are innumerable and side by side, one merging into the next. We therefore see a band of colour, from red to violet, as we rotate the telescope about the axis of *G*, which is really made up of numberless images

## THE SPECTROSCOPE

slit, each image of a slightly different colour. If, instead of using a white light as the source of illumination the slit, we used a Bunsen burner in which some sodium salt was being burnt, we should see a very dull, more or less continuous spectrum, but one exceedingly bright yellow line, whose wave-length is approximately  $5893 \times 10^{-8}$  centimetres. The term 'approximately' is used because, with a reasonably good spectroscope and narrow slit, we should see *two* fine yellow lines, of wave-length  $5890.2 \times 10^{-8}$  centimetres and  $5896.2 \times 10^{-8}$  centimetres respectively. Every burning metal gives a different line or set of lines; thus a potassium

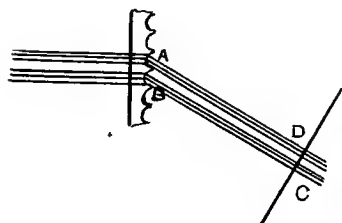


FIG. 11.

salt placed in the flame would show a deep violet line and a deep red line; a thallium salt would show a bright green one, and so on. Gases under reduced pressure, through which an electric spark from an induction coil is passed, give sets of lines similarly.

It is by examining such sources of illumination, and determining the wave-lengths of the principal lines in the observed spectra, that chemical spectrum analysis becomes possible. This subject will, of course, be taken up very fully in subsequent chapters.

Although throughout this chapter we have looked upon the diffraction grating as a series of transparent and opaque lines ruled upon glass, this is not really the case, and a further description now becomes necessary. A *plane grating* is a piece of perfectly flat glass, ruled on one side with a series of fine lines an equal distance apart; this is done by means of a diamond point and a very elaborate ruling machine. In Fig. 11, let A and B be two of these rulings, and let CD be a screen placed perpendicularly to the diffracted waves, the

distance between CD and the grating being so great that all the waves from B to C may be said to travel a distance  $BC - d$ ,  $d$  being the difference between successive paths from the ruling to CD. As  $d$  depends on the nature of the rulings, it is the same for each ruling, and hence the difference in phase between the resultant vibrations of each groove is  $(BC - d) - (AD - d) = K$ , or  $BC - AD = K$ , a constant for the angle which BC, AD, etc., make with the grating. By previous reasoning, then, when  $K$  = an even number of half wavelengths, the waves travelling along BC, AD, etc., are in the same phase, and a bright image results on bringing them together by means of a suitable lens.

Rulings have also been made upon concave spherical mirrors, and a spectrum is obtained by having the slit and observing eye-piece on the circumference of a circle, of which the diameter is a radius of the curvature of the concave grating. If  $\theta$  be made equal to  $O$ , in the equation

$$\lambda = b (\sin \theta - \sin \phi)$$

we have

$$\lambda = b \sin \phi,$$

and  $\theta = O$  when the spectrum is observed normal to the grating. If  $\theta = O$ , the relation is also true that

$$n \lambda = b \sin \phi;$$

hence if  $n$  be small,

$$n\lambda_n = b \sin \phi, \text{ and}$$

$$2n\lambda_{2n} = b \sin \phi$$

or  $n\lambda_n = 2n\lambda_{2n}$ . This means that, overlapping some such line as  $\lambda = 6000 \times 10^{-8}$  centimetres in the second order spectrum, there will be another line  $\lambda = 3000 \times 10^{-8}$  centimetres in the first order spectrum. This property of the arrangement of the concave grating has been utilized very largely in making accurate wave-length determinations.

## CHAPTER II

The prism spectroscope—Different forms of apparatus—Slits, lenses, and prisms—The spectrometer—Direct-vision spectroscopes—Methods of reading the angular deviation of a coloured ray—Plane gratings and replicas.

A *PRISM SPECTROSCOPE* suitable for laboratory work consists essentially of a slit, collimator, prism, and telescope, and some means of determining the angular deviation of the telescope when any portion of the spectrum (or any bright line in a line spectrum) is viewed in the centre of the field of its eye-piece.

It would thus seem that all spectroscopes would be much alike in pattern, but this is by no means the case, and an efficient instrument must possess many working details which necessitate description.

The *slit* of the *spectroscope* should be adjustable—*i.e.*, should be capable of being made narrower or wider. A bright line seen in a spectrum is, as already explained, an image of the slit, and as we want to resolve any line such as the yellow sodium line into its constituents if it be not actually single, the slit must be very narrow; otherwise two closely adjacent images would overlap, and only the one line would be seen. As fine a line as possible is also required to accurately measure the angular deviation of the telescope when that line is focussed on the cross-wires in the eye-piece; this fact will be readily appreciated if we look at Fig. 12. Let C and D be the jaws of the slit, and S the screw for opening or closing it. As a general rule, one *jaw* of the *slit*, C, is fixed,

and the screw S actuates the other jaw, D. Suppose now that the distance between C and D be  $r$ , and we see a bright line in the telescope of width  $R$ . The cross-wires in the eye-piece are focussed upon the centre of the line, which therefore projects  $\frac{R}{2}$  each side of the centre of the field. If now the slit be so nearly closed that the width is very small,  $=t$ , and the bright line seen in the telescope is infinitely narrow, both sides of the slit will nearly coincide, and hence

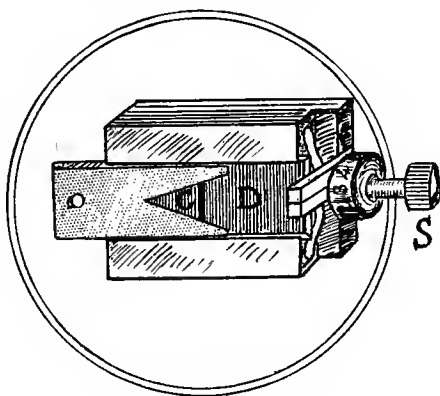


FIG. 12.

each side of the line will be  $\frac{R}{2}$  nearer to the centre of the field than when the slit was wider open. As C is fixed, and D moves further from C according as the slit is opened, the centre of the wide line would be a distance  $\frac{R}{2}$  too much to one side when the width of the slit was  $r$ .

The screw S should preferably be fitted with a divided drum-head, as shown in the figure, so that some measurement can be made of the width used at any time. The jaws should be made of untarnishable metal, so that chemical fumes will not attack them, and great care should be taken not to quite

close the slit at any time. If dust gets between the jaws—and it will cause dark lines across the length of the spectrum if it does—the slit should be opened wide enough to take the point of a piece of soft wood, pointed like a pencil, then gently closed until the jaws press lightly upon it, and the wooden point gently worked up and down once or twice, and not withdrawn until the slit has again been opened.

A *sliding V-shaped wedge* is usually attached to the slit, by means of which the width of the aperture can be altered. Another adjunct is the *comparison prism*, which enables two different spectra to be examined simultaneously. The jaws are sometimes made of *platinoid* and sometimes of *quartz*. Hilger supplies a pair of quartz jaws for a slit up to 1.5 centimetres for £3. A very fine and accurate edge to the jaws can be obtained in the case of quartz, and its transparence does not interfere, since the edge is cut obliquely, and hence each edge is a prism, which refracts the rays which pass into it, so that they do not reach the collimating objective.

As it is essential that the jaws be parallel, screws should be provided to correct any want of parallelism which may occur after some time. When the slit is practically closed, the line of light should vanish, whilst if the jaws are not parallel it will appear slightly wedge-shaped. Correction of this fault is a delicate matter, and should be done with extreme care.

*The Comparison Prism.*—This is a small right-angled prism which can be swung out of place when desired. A ray of light from P (Fig. 13, A) suffers total reflection from the prism at R, and enters the slit S, travelling along ST. The comparison prism is very small, and only covers half the slit (Fig. 13, B), so that light from one source, Q, normal to the collimator can be compared with light from another source, P, perpendicular to the axis of the collimator.

As regards the greatest *width of slit permissible* for perfect resolution, it can be shown from physical considerations that

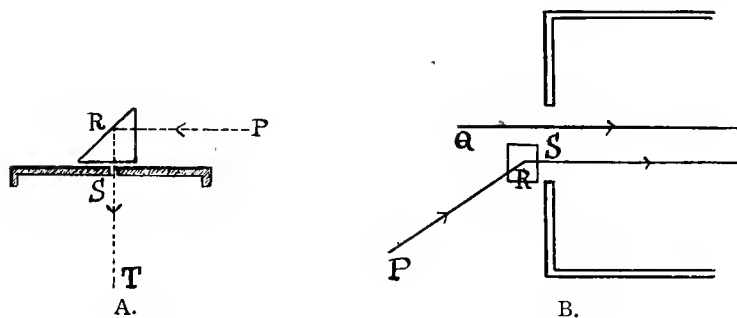


FIG. 13.

if  $\phi$  be the angle subtended by the collimating lens at the slit,

$$d = \frac{\lambda}{4\phi},$$

where  $d$  is the width sought. As  $\phi$  is more or less  $\frac{1}{16}$ , we see that the slit need not be less in width than four wave-lengths of the ray under examination.

The light from the slit travels to the collimating lens, and emerges parallel from it, the distance between lens and slit being made equal to the focal length of the former. It is very necessary that the collimator be *achromatic*, as with a plain uncorrected lens the focal length varies for light of different wave-lengths—*i.e.*, rays of different colours. The collimating telescope C (Fig. 14) is firmly fixed to the stand, whilst the telescope T, which should also be fitted with achromatics, is movable round the divided circle D, and T is always a radius of a circle whose centre is the centre of the *prism table* P. M is a clamp for fixing the telescope to the circle, and F is a fine adjustment of the tangent form. The prism is clamped by some suitable arrangement to the table P, and P itself should be capable of rotation, and some means provided of

measuring any angle through which it is turned. A vernier, V, travelling with the telescope round the divided circle enables angular measurements to be taken. The circle is usually divided in half-degrees, whilst the vernier reads to one minute or thirty seconds of arc.

It is very desirable that the *prism table* P be fitted also with a vernier, so that its position can be accurately ascertained.

A spectroscope of the construction thus briefly discussed

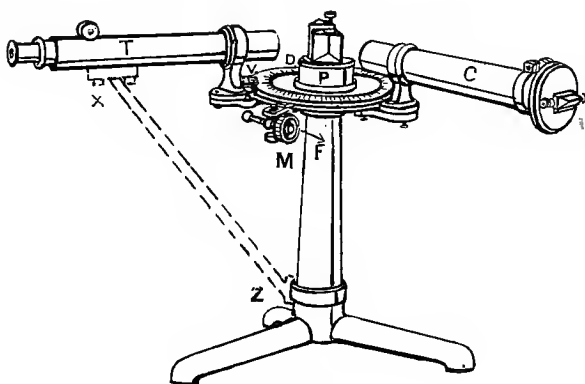


FIG. 14.

is suitable only for ordinary qualitative work, and many elaborations of the simple instrument are required to make an accurate instrument. One important improvement is shown in Fig. 14 by the dotted lines; these represent a support for the telescope, which is fixed to the latter at X, whilst at Z it terminates in a U-shaped end, which fits on to a metallic ring of rectangular section, which is fastened to the pillar of the instrument. This support, which must be nicely and accurately made, and which must work very smoothly at Z, renders the telescope quite rigid. Many of the more massive instruments have such a support, whilst others are



arranged still better, the telescope being supported quite independently of the divided circle, as will be seen presently.

We shall diverge at this point to describe the lenses and prism. Beyond the violet end of the spectrum is the *ultra-violet region*, which is invisible to the eye, but may be examined by photographic means, or with a fluorescent eye-piece (see later). Beyond the red end of the spectrum is the *infra-red region*, which is also invisible, but may be examined by photographic or bolometric means. Now if much work is to be done in the ultra-violet, lenses of quartz must be used, since ordinary flint and crown glass absorb the majority of rays of short wave-length; similarly, a quartz or calcite prism will also be required.

But for general work it will suffice to have good *achromatic lenses* of crown and flint glass, made in the ordinary way, and one or more prisms of dense flint, the refractive index of which, for the yellow sodium line, varies between 1.57 and 1.96. The greater the refractive index, the greater the dispersion—*i.e.*, the angle between two rays of fixed wave-length; hence as dense a glass should be chosen as possible, so long as it be not too yellow in colour, when it will begin to interfere seriously with the passage of the violet rays.

Two *conditions for efficiency* are that the collimating lens must be completely filled with light (which is the case when the slit is a distance from it equal to its focal length), and that the whole of the face of the prism must be illuminated by the parallel rays emergent from the collimator. This means that if the collimator be fitted with a lens of  $1\frac{1}{4}$  inches clear aperture, the prism face should be  $1\frac{3}{4} \times 1\frac{1}{4}$  if the usual  $60^\circ$  prism be employed.

The eye-piece of the telescope deserves some consideration at this point. The cross-wires, which are used for obtaining the position of the line measured, will not be visible in the case of a dark spectrum or one containing only a few bright

lines. Some method of illuminating the wires is therefore necessary if this method of wave-length determination be adopted. The Gauss eye-piece, as made by Hilger, is of the Ramsden construction, containing a plane mirror inclined at about  $45^\circ$  to the optic axis, and placed between the two lenses (of which the eye-piece consists). Light can enter

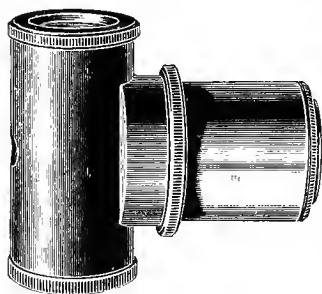


FIG. 15.

an aperture in the side of the tube, and is reflected from the mirror on to the spider-webs or cross-wires, which therefore renders them visible.

W. Wilson also makes an excellent eye-piece attachment, which is fitted over the eye end, and gives a soft illumination of the entire field. It is shown attached to an eye-piece in Fig. 15.

The price is only a few shillings, and it will be found very efficient.

The most common form of prism spectroscope is fitted with one prism, each angle of which is  $60^\circ$ , and the top and bottom of the prism, and one side, have their surfaces ground. Greater dispersion is obtained by means of two prisms than one, but for general analytical work one is preferable, of as large a size as is appropriate for the lenses of the instrument. It is the custom with some workers to alter the prism every time the angular deviation of a ray is measured, so that it is in the position of minimum deviation for that ray; this is necessary, furthermore, in the case of calcite prisms. Hence the cheaper instruments fitted with two prisms are less desirable than those fitted with one large one.

Very frequently an instrument with which the angular rotation of the prism table, as well as of the telescope, can be measured is called a spectrometer, but we shall use the

term 'spectroscope' in all cases, as, to be of any use, one must necessarily be the other, except in very special forms of instruments.

In order to read off the angular deviation of the telescope by means of the *vernier* more accurately, some form of *reader* is required; a simple magnifying-glass is usually provided with a cheap instrument, but a small microscope attached to a movable arm, which rotates about the centre of the divided circle, forms a part of all ordinary instruments. More often two verniers are provided, one at each end of a diameter

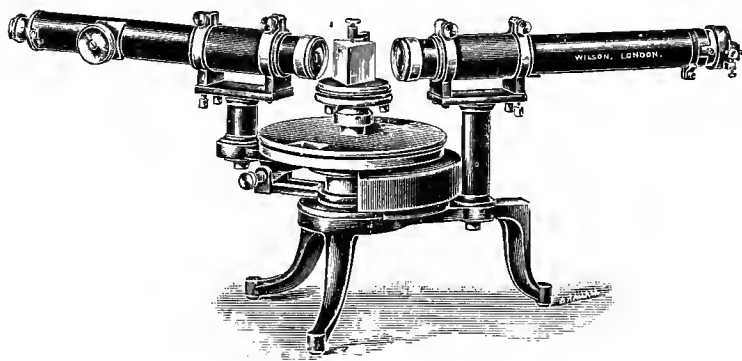


FIG. 16.

of the divided circle, and in this case two microscopes are similarly provided. It is far better to have the two verniers and readers if possible, as the two readings obtained form a check on irregularities or faults in the dividing of the circle. Hilger's *auto-collimating goniometer* is fitted with two microscopes underneath, and parallel to the telescope collimator, and thus the readings can be made without moving from the observing position. A good light should be used to illuminate the divided circle whilst the readings are being made, a small movable electric lamp being very serviceable for this purpose.

One very popular instrument, which is capable of good general work, and is very reasonable in price, is shown in

Fig. 16. Here the collimator is supported on an iron upright independent of the divided circle. The telescope is counterpoised by a heavy iron weight, and revolves about the central pillar. The telescope has a clamp and fine adjustment, and a vernier reading against a fixed divided circle to one minute or thirty seconds of arc.

For analytical work, such as will be chiefly considered in this book, a fairly massive spectroscope, with  $1\frac{1}{4}$ -inch lenses

and a 2-inch dense flint prism, having the telescope either counterbalanced by a weight or supported by a stay as suggested in Fig. 14, will be found efficient. Though the prism table should be capable of rotation, it will be found to suffice for general qualitative work to have the prism fixed in the position of minimum deviation for some green ray (*i.e.*, a ray of wave-length

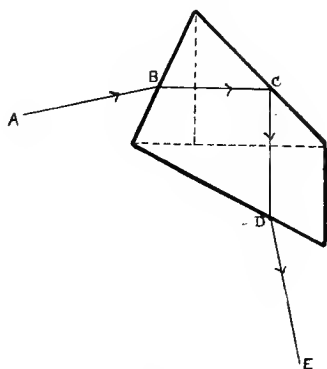


FIG. 17.

intermediate between the least and most refrangible rays measured).

A special instrument for wave-length determination only is known as the *constant deviation* spectroscope.

In a very popular instrument of this type made by Hilger we find the collimator and telescope fixed permanently at right angles, and it is, therefore, a *fixed-arm* spectroscope. The *prism* is rotated in order to pass through the spectrum, and the advantage of this method is that each spectrum ray is viewed in the angle of minimum deviation.

The prism calls for explanation. Though made actually in one piece, it may be considered as made up of three prisms, as shown in Fig. 17. A ray of light, AB, from the collimator

meets the first prism, whose angles are  $30^\circ$ ,  $60^\circ$ ,  $90^\circ$ , in the minimum deviation position, so that it is refracted along BC, parallel to the prism base. It enters the next prism (a  $45^\circ$ ,  $45^\circ$ ,  $90^\circ$  prism) normal to the face, and thus passes undeviated along ~~CD~~<sup>CE</sup>, meeting the next face at an angle of  $45^\circ$ , where it is reflected, therefore, at an angle of  $45^\circ$ , passing normally through the third face and entering the next prism, whose angles are  $30^\circ$ ,  $60^\circ$ ,  $90^\circ$ , parallel to its base, and therefore, as it were, in the position of minimum deviation, whence it emerges along DE and enters the telescope.

The most ingenious part of the instrument is a carefully divided drum, which, when turned, rotates the prism table; this drum is so divided that on it are read the wave-lengths direct, so that no calculations are necessary. Thus, if the green mercury-line be seen in the centre of the eye-piece, the reading on the divided drum will show the wave-length to be 5461 A.U.

A more massive form of the fixed-arm wave-length spectroscope has recently been introduced by Hilger, and it is a very precise and convenient instrument. The extra dense prisms are strongly to be recommended, as the dispersion in the red end of the spectrum is so much better that higher accuracy is obtainable.

The constant deviation spectroscope requires careful adjustment, and when once adjusted, care should be taken not to interfere with the prism. The spectroscopes are sent out with lines scratched on the prism table, to indicate just where the prism is to be placed. Having put it in this position, a known line should be examined, and the divided drum turned until the pointer indicates the wave-length of this line. The line will most probably lie slightly to one side of the cross-wires, possibly much to one side. The prism is then gently moved by tapping until the line comes practically upon the intersection of the cross-wires; it is then brought

precisely into the centre of the field by turning a small adjustment screw provided at the eye end of the telescope. Another known line must now be examined, and the reading on the drum should give the wave-length correctly; if it does not, the prism must be slightly shifted. The correct position is thus obtained eventually by the trial by error method.

*Auto-Collimating Instruments.*—It is possible to make one telescope answer the double purpose of collimator and viewing telescope, and an instrument more especially designed for the measurement of angles is made by many

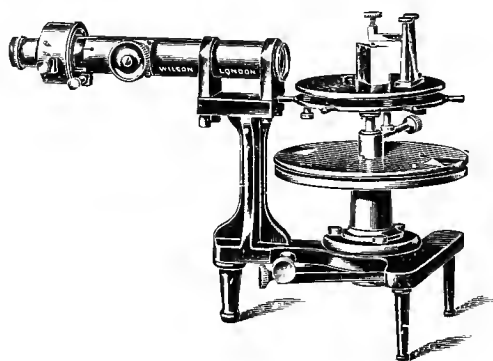


FIG. 18.

firms on these lines. Such instruments are known as auto-collimating spectrosopes, or goniometers, etc. Hilger and Zeiss make excellent instruments of this pattern, but quite an efficient one is obtainable from W. Wilson, at a very low cost of something like £6, which is provided with an objective of  $\frac{15}{16}$  inch diameter, of a focal length of about  $8\frac{1}{2}$  inches. It is seen in Fig. 18. The light enters a slit in the side of the telescope tube (Fig. 19), and is reflected by a small prism along the tube to the lower half of the lens L, whence it emerges parallel, and falls upon the face of a  $30^\circ$  prism, set in the angle of minimum deviation for a certain ray. It therefore meets normally the opposite face AB, which is

silvered. The ray, therefore, travels back along its original path, and is seen in the upper half of the eye-piece. Only light of one wave-length can, of course, meet the prism at minimum deviation; hence a spectrum is produced and is

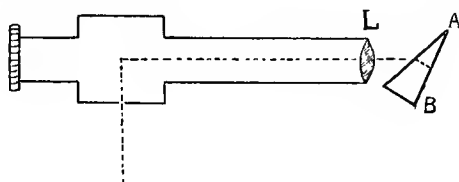


FIG. 19.

seen in the eye-piece. The spectroscope made by Wilson possesses a prism table capable of adjustment by three levelling-screws, and it has a clamp and fine adjustment by

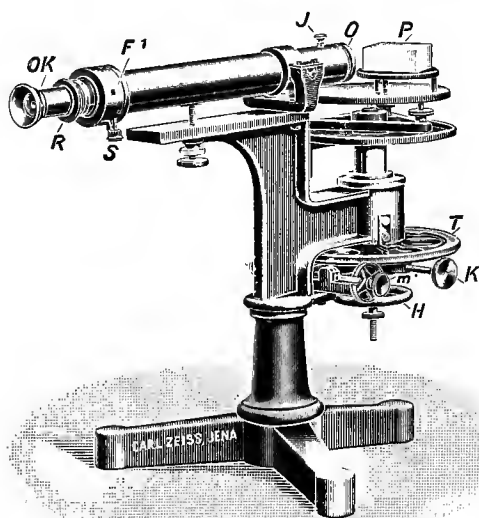


FIG. 20.

tangent motion, two verniers being provided at each end of a diameter, and the divided circle being protected. In order to find the angle of a prism, the prism table is turned

until the reflection of the slit from one face is seen coincident with the pointer in the eye-piece. The angle  $\theta$  of the prism table is then read. The prism table is now turned until the slit is again seen, reflected from the opposite face, and the angle  $\phi$  read on the divided circle. The angle between the two faces is then given by subtraction, and  $= \phi - \theta$ .

The auto-collimating spectroscope of Zeiss is a very fine

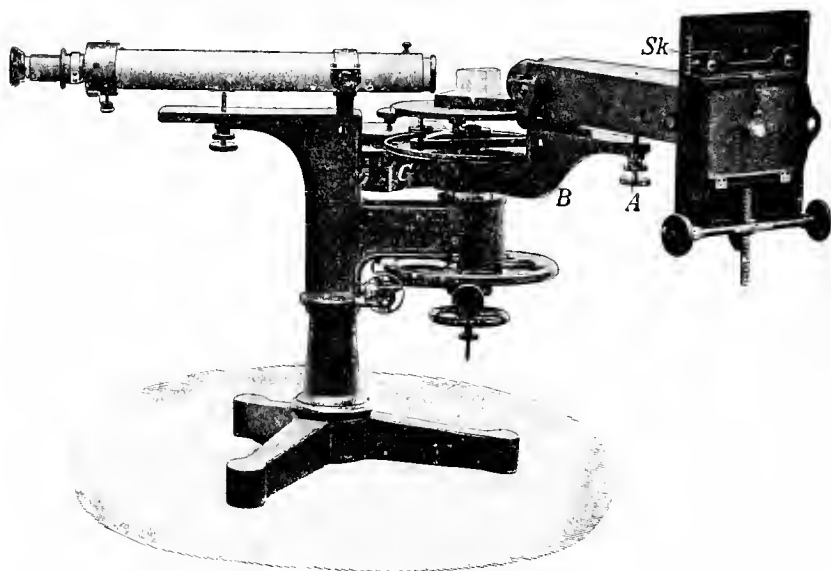


FIG. 21.

instrument, depending for the dispersion on a compound prism. The arrangement is seen in Fig. 20. The light from the source to be examined enters at *F*, and is deviated by reflection in a small prism along a path at right angles, collimated by the lens *O*, and then meets the face of the prism *P*. The light is reflected from the face back along its own path, and re-enters the objective. One ray alone can, of course, travel back exactly the incident path, hence a spectrum is produced.



The spectroscope may be converted into a *spectrograph* by the substitution of an ordinary prism, and a counterpoised light metallic camera. The spectrograph is seen in Fig. 21, where also many movements are shown which we have not space to describe in the text.

If a combination of two equal prisms be taken, one in the

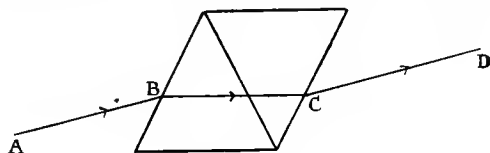


FIG. 22.

opposite position to the other as regards their bases, a given ray of light will eventually emerge through the combination unaltered in direction—*i.e.*, its path will be parallel to its original path. Thus, in Fig. 22, if AB be the ray, the emergent ray CD will travel a path parallel to AB. But if now the two prisms be of different substance, such that their refractive indices are the same for light of one wave-length,  $\lambda_x$ , but different for light of other wave-lengths, the



FIG. 23.

only ray which will emerge parallel to its original path is the one whose wave-length is  $\lambda_x$ ; all other rays will emerge somewhat refracted.

On this principle the *direct-vision spectroscope* is constructed, a diagram of which is shown in Fig. 23. Three or five prisms are usually used, made of crown glass and flint glass, of such refractive indices that one mean ray will be undeviated by its passage through the combination, whilst all other rays will be deviated. In the figure S is the slit of the

spectroscope, C a collimating lens, P the combination of prisms, and E the eye-piece. Most of such *direct-vision spectroscopes*, as they are called, have an adjustable slit at S, and a sliding-tube so that the distance between S and C can be adjusted until the lines in a spectrum are in distinct focus.

If we assume the refracting angles of the prisms to be very small, then, considering a ray at minimum deviation, we have—

$$\mu = \frac{\frac{\beta + d}{2}}{\frac{\beta}{2}},$$

$$\text{or } d = \beta(\mu - 1).$$

If  $\mu_m, d_m$ , be respectively the refractive index and angle of minimum deviation of one prism for a ray of wave-length  $\lambda = m$  and  $\mu_n, d_n$  the same for a ray of wave-length  $\lambda = n$ , then we have—

$$d_m = \beta (\mu_m - 1), \text{ and}$$

$$d_n = \beta (\mu_n - 1), \text{ and}$$

$$\frac{d_{m+n}}{2} = \beta \left( \frac{\mu_{m+n}}{2} - 1 \right),$$

for the mean ray. The dispersive power is therefore expressed by—

$$\frac{d_m - d_n}{\frac{d_{m+n}}{2}} = \frac{\mu_m - \mu_n}{\frac{\mu_{m+n}}{2} - 1}.$$

The *dispersive powers* of some substances are given below :

Water	-	-	0.042
Crown glass			0.043
Flint glass	-		0.061

The angles of the prisms could be chosen such that the dispersion produced by each was the same. But if the angles of two prisms be chosen so that the *deviation* of a

given mean ray produced by each is the same, but the *dispersion* of each is *different*, the mean ray would be undeviated, but the rays on either side of it would be deviated; hence a spectrum would be produced at direct vision.

The direct-vision spectroscope is more or less of an instrument for rough qualitative work, but some large patterns are made with which approximate wave-length determinations can be made. One interesting little instrument is made by Zeiss, in which a scale of wave-lengths is seen across the spectrum; the scale of course only divides the spectrum into



FIG. 24.

large areas, but by its means the approximate positions of absorption bands, etc., can be found.

Another method of measurement is by means of a *travelling slit*, which can be moved by a micrometer screw, so that different parts of the spectrum can be brought into the centre of the field. Such an instrument is made by Hilger, a finely divided drumhead being provided with micrometer screw motion and a fixed pointer in the eyepiece, these arrangements 'enabling wave-length determinations to be made with considerable accuracy' (Fig. 24).

We have also to consider the *photographic scale* method of

determining the position of any line in the spectrum, as this is used in many smaller patterns of prism spectroscopes, and sometimes in direct-vision instruments. The principle is seen in Fig. 25. Here C is the collimator and T the telescope; S is a third tube, illuminated at L by some source of white light, and possessing a photographed scale, an image of which is cast upon the prism face AB, and thence reflected into the telescope; consequently one sees, when examining the spectrum, a scale overlapping it, and by means of this scale the position of a line or region can be determined in a relative sense only. Thus in a given

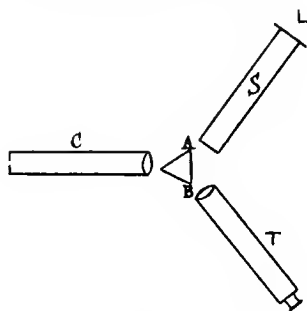


FIG. 25.

instance the red line of a hydrogen vacuum tube might have a position on the scale of 33.5, and the blue hydrogen line a position of 91.5, and so on. If, then, on examining an unknown vacuum tube a red and a blue line were seen in its spectrum occupying these respective positions, it could be concluded that the tube contained hydrogen.

In practice it has been found that a shifting of the scale relatively to the spectrum is liable to occur, which would of course throw everything out, and the photographed scale method is, therefore, never used for accurate work.

*The Comparison Spectroscope.*—This is an instrument designed for roughly comparing the absorption spectra of

two fluids or coloured translucent objects. A very convenient form is made by Zeiss, the principle of which is seen in Fig. 26. Here *F* is the stage of the instrument, with two openings,  $G_1$  and  $G_2$ , which are illuminated (as in a microscope) by two mirrors (not shown) underneath the stage. Over these openings are placed cells containing the fluids to be compared, and the light from each is

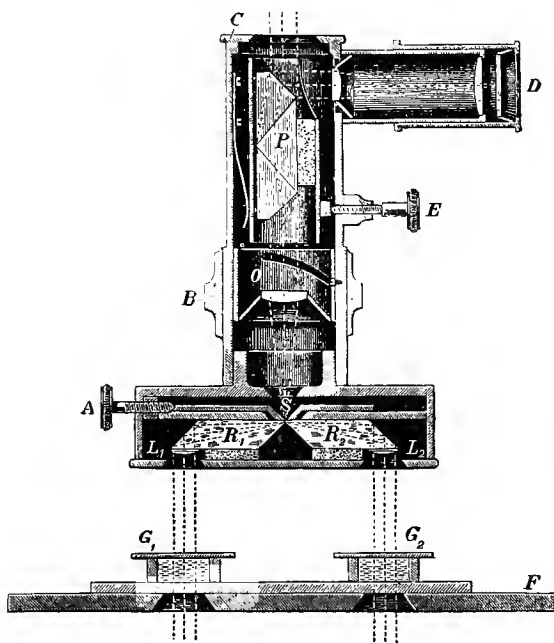


FIG. 26.—COMPARISON SPECTROSCOPE FOR LABORATORY USE.  
Upper body in section. (Two-thirds full size.)

reflected, by means of the special prisms  $R_1$  and  $R_2$ , into the slit *S*. The eye is placed at *C*, and it sees the two spectra side by side—*i.e.*, one above the other—whilst a photographed scale of wave-lengths is also thrown on to the spectra by means of the side-tube, which is illuminated at *D*. Zeiss also makes now a similar instrument for the

simultaneous examination of three spectra. A noteworthy accessory is a cell, which is provided with a micrometer arrangement for varying the height of the coloured liquid; this is useful when comparing two absorption spectra; the movement reads to  $\cdot 05$  millimetre—*i.e.*, the height of the column of liquid through which the light passes before entering the slit can be measured to  $\cdot 05$  millimetre. The metal parts of this 'absorption vessel,' which come in contact with liquid, are of nickel.

The preliminary adjustment of the instrument is carried out as follows. By turning the milled ring B in Fig. 26 the lens O is focussed until the bright lines in a known spectrum (*e.g.*, the Fraunhofer lines in daylight or the lines from a vacuum-tube spectrum) are seen quite distinctly. The width of the slit is regulated by the screw A. The wavelength scale can then be brought into perfect adjustment with the lines and locked in position. The two prisms  $R_1$  and  $R_2$  are provided with lenses  $L_1$  and  $L_2$ , whose focal length (measured in glass) is equal to their distance from the slit; hence only parallel rays enter the slit.

By means of such a comparison spectroscope the position and limits of absorptions may be conveniently measured by illuminating one-half of the slit with a source of illumination giving several known lines, and the other half of the slit with the coloured substance under examination. The scale need not, therefore, necessarily be used.

Although *plane diffraction gratings* are somewhat difficult to obtain, and are very expensive, such good copies of them can nowadays be bought, in celluloid, that they are capable of really accurate general work. These *replicas*, which are prepared by Thorp and others, are mounted on special flat plate glass, and vary in price from 15s. upwards. If the collimating lens be of  $1\frac{1}{4}$  inches aperture, the replica itself should obviously be at least  $1\frac{1}{4}$  inches square, and

preferably a trifle larger. Such a replica, with about 15,000 lines to the inch, will give a resolving power of at least 18,750 (see Chapter III.), whilst a resolving power of only 982 is required to separate the yellow sodium lines.

The dispersion produced by a grating is such that the light is diffracted proportionally to its wave-length, and hence a normal spectrum is produced; the orange and red portions of the spectrum are thus very much better proportioned than in the prismatic spectrum, whilst the blue-violet region is more cramped, but thereby more brilliant.

In order to use a grating replica a holder is necessary, which must be substituted for the prism clamp used ordinarily

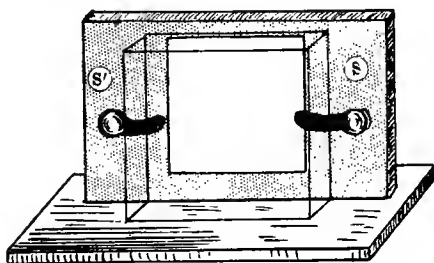


FIG. 27.

on the prism table. Such a holder is shown in Fig. 27, where the plane grating replica is held close against the vertical frame by the spring clips S, S'. The base of the holder is fastened to the prism table by means of two upright screws.

It is very desirable to be able to rotate the grating, whose plane should pass through the centre of the prism table, and an ordinary spectrometer will answer the purpose. If the grating be set normally to the collimator axis, and the first order spectrum used, the wave-length of any line is measured by the expression—

$$b \sin \theta,$$

whence the angular deviation  $\theta$  of the telescope at once furnishes the necessary details for determination.

An excellent *wave-length spectroscope*, the telescope of which is read by means of a micrometer screw which works on a sine motion, is made by Beck, a sketch of which is seen in Fig. 28. The instrument consists of a large collimator, a

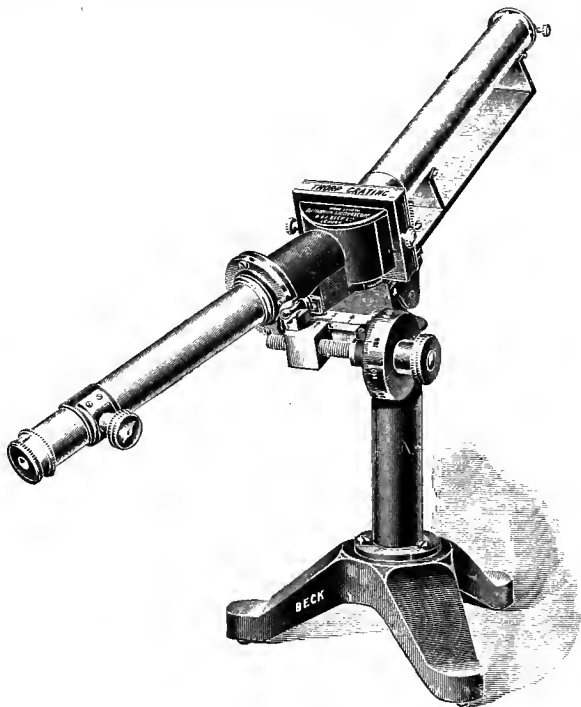


FIG. 28.

plane grating (replica), and the telescope; the latter is moved by a micrometer screw, which gives the readings  $b \sin \theta$  direct. The whole of the adjustments are so arranged that they can be checked and readjusted, which is a great convenience.

*Prisms and grating replica combined* can be obtained also,



the angle of the former being so arranged that the spectrum is seen almost at direct vision, or that the mean ray emerges parallel to the axis of the collimator. Very great dispersion is obtained by means of these combinations; and since the production of the grating replicas has been practically perfected, they are strongly recommended where the spectroscopic itself is of a sufficiently rigid pattern to warrant their use.

The prism gratings supplied by Beck are, as already stated, so arranged that the mean ray of the visible spectrum is hardly deviated; but a replica may just as easily be cemented



FIG. 29.

to a  $60^\circ$  prism, when enormous dispersion will be produced, although the collimator and telescope will then be at an angle.

A very neat little pocket direct-vision spectroscope is prepared on the prism-grating plan, which costs only a few shillings, and is a useful adjunct to the laboratory; it is quite delicate enough to pick out the chief Fraunhofer lines (*q.v.*), and to distinguish the lines in ordinary flame spectra.

A more elaborate instrument of this type is shown in Fig. 29. An illuminated arrow-point is seen at the top of the spectrum, and a graduated revolving milled head moves this point along the spectrum, thus enabling the position of any line to be registered.

The visible spectrum is divided into 500 divisions by means

of the graduations, and by finding out what readings correspond to two known lines the relation between the graduations and wave-lengths is readily ascertained. .

When working with a plane grating, the combined width of a ruling and the space between it and the next ruling will be required, and this is denoted by  $b$ , which is in metric measure.

Suppose the grating have 14,450 lines to the inch. Then, since

$$1,000 \text{ mm.} = 39.37043 \text{ inches,}$$

$$1 \text{ inch} = \frac{1}{39.37043} \text{ mms.}$$

$$\therefore b = \frac{1}{39.37043 \times 14450} \text{ mm.}$$

$$\text{or } b = .0017577 \text{ mm.}$$

Hence, if the angular deviation for a certain line were found to be  $19^\circ 18'$ , with the plane grating normal to the collimator, the wave-length would be found from

$$\lambda = b \sin 19^\circ 18',$$

$$\text{or } \lambda = .0017577 \times .3305 \text{ mm.,}$$

$$\text{or } \lambda = 5809 \text{ A.U.}$$

The general data for the method will be found in the next chapter.

## CHAPTER III

Adjustment of the spectroscope—Measurement of the refracting angle and the index of refraction of a prism—Measurement of the width of a grating ruling—Refractive indices of liquids—Change of refractive index with change of solvent—Molecular refractive power—Additive nature of atomic refractive powers of elements—Resolving power of prisms and gratings—Absorption by prisms—Anomalous dispersion.

CERTAIN conditions have to be observed in setting up a spectroscope before it is used. The rays of light which emerge from the collimator must be parallel; the slit must be parallel to the refracting edge of the prism—*i.e.*, both must be absolutely vertical; and where a grating or grating replica is employed as the dispersing medium the rulings must be perfectly parallel to the slit.

The slit is fixed at the focus of the collimating lens in some instruments, but as a general rule it is not. In order to adjust the collimator, therefore, the following procedure is carried out: The eye-piece of the telescope is adjusted so that the cross-wires are distinctly seen. The telescope is then directed towards some distant tree, church spire, or chimney, etc., and the eye-piece racked out until it is quite distinctly seen. The distant object may be looked upon as being infinitely distant, so that parallel rays are incident upon the objective. The telescope is then turned so that it is in a straight line with the collimator, and the slit, which is now illuminated by some convenient light source, can be seen exactly in the centre of the eye-piece, crossing the inter-

section of the cross-wires or spider-webs. The draw-tube of the collimator is then drawn (or racked) out until the image of the slit is absolutely distinctly seen. The slit should be opened to different widths and examined at each, as this makes it easier to be quite sure when the image is perfectly distinct. Many collimator tubes are provided with a collar and screw, which enable the draw-tube to be fastened quite tightly when once the requisite position has been found. The slit must, of course, be vertical, and its centre must appear at the intersection of the cross-wires. Compensating screws are usually provided, by means of which the telescope and collimator can be corrected if their optic axes do not lie along one straight line.

The prism is next placed on the prism table, which generally has three levelling-screws, by means of which the refracting edge of the prism and the slit can be got into the same plane and perfectly parallel. A certain line, such as the yellow sodium or the green mercury line, should be brought into observation by illuminating the slit with the necessary light and turning the prism table until the ray chosen is at the angle of minimum deviation. The telescope is then very slightly turned in one direction, so that the bright line appears slightly to one side of the centre of the field; the prism is now rotated until the bright line again comes into the centre of the field, and then rotated in the opposite direction until it is again seen there, these two positions being possible, as can readily be seen from an experimental observation. The line should appear equally sharp with the prism in both positions if the rays from the collimator are perfectly parallel; it should also appear absolutely vertical if the refracting edge of the prism has been properly adjusted.

#### MEASUREMENT OF THE REFRACTING ANGLE OF A PRISM.

—The prism is placed on the prism table, and the refracting

edge is turned towards the collimator. The telescope is now turned in one direction until the image of the slit is seen by reflection from one face of the prism, the slit being centred on the intersection of the cross-wires—*i.e.*, being seen in the exact centre of the eye-piece. The angular deviation  $\theta$  of the telescope is then read. The telescope is now turned in the other direction until the slit is again seen owing to reflection from the other prism face; the new angular deviation  $\phi$  is read. The difference between  $\theta$  and  $\phi$  gives the required angle. White light may, of course, be used in this measurement, which simply depends on reflection.

MEASUREMENT OF THE REFRACTIVE INDEX OF A PRISM.  
—The refractive index,  $\mu$ , varies with every ray used in its measurement. Thus,  $\mu$  measured with the yellow sodium line will be different from  $\mu$  obtained with the green mercury line, and so on. The following table gives  $\mu$  for crown glass and monobromnaphthalene for different rays :

	Wave-length of Light used.		
	$\lambda = 6563.$	$\lambda = 5893.$	$\lambda = 4861 \text{ A.U.}$
Crown glass	1.531	1.534	1.540
Monobromnaphthalene -	1.644	1.658	1.681

To obtain the refractive index the prism is set in the approximate position of minimum deviation for a certain ray; if a sodium flame be used, the D line will answer very well, and is indeed most frequently used. The prism is now very carefully adjusted for minimum deviation by slowly rotating the prism table until further *slight* rotation in either direction leaves the line unshifted. The angular deviation is then determined by the telescope vernier reading, and the angle of the prism is, of course, already known. We have

merely, therefore, to substitute the values for  $A$  and  $\theta$  in the formula—

$$\mu = \frac{\sin \frac{A + \theta}{2}}{\sin \frac{A}{2}}.$$

If a  $60^\circ$  prism be used, this becomes—

$$\mu = \sqrt{1 - \sin^2 \frac{\theta}{2}} + \sqrt{3} \cdot \sin \frac{\theta}{2}.$$

The value for  $\mu$  thus obtained is relative to air, and it will be shown later how such value may be made absolute.

The variation in the refractive index for light of the same wave-length varies with rise of temperature, and some liquids are particularly susceptible to the change. Thus carbon disulphide is unsuitable for a liquid-dispersing medium, as the change in  $\mu$  for a small change in temperature ( $\frac{d\mu}{dt}$  expressed differentially) is great compared with other more suitable liquids. But under no circumstances is a 'liquid prism' suitable for general work.

The *absolute refractive index* of a substance, which must be determined in making comparisons of the optical properties of different media, is the value of  $\mu$  for the substance when all air is removed—*i.e.*, when the apparatus is *in vacuo*. The absolute refractive index of air at 76 mm. pressure and  $0^\circ$  C. —*i.e.*, at n. t. p.—is about 1.00029. Hence the refractive index of a substance ascertained in air in the ordinary way, at n. t. p., is multiplied by this factor to obtain the absolute refractive index.

When *quartz prisms* are used for spectrographic work in the ultra-violet, or in a spectroscope fitted with a Liveing fluorescent eye-piece, it must be remembered that they are cut from the piece of crystal in such a way that the rays of

light which enter them travel along their optic axis, in order to avoid double refraction. There is one axis in quartz and other uniaxal crystals along which no double refraction takes place, and this is termed the optic axis; in a uniaxal crystal, cut perpendicular to the optic axis, all normal rays of the same wave-length travel with the same velocity; in other words, uniaxal crystals have all their optical properties symmetrical about one direction—viz., the optic axis.

**DETERMINATION OF THE RULING WIDTH,  $b$ , IN A PLANE DIFFRACTION GRATING.**—The grating is mounted on the prism table in a suitable holder, and placed as nearly normal to the optic axis of the collimator lens as can be judged, and then a perfect normality obtained by experiment. A bright line, of wave-length  $\lambda$ , is examined, with the telescope inclined one way, then the same line is examined with the telescope on the opposite side of the collimator axis. The angular deviations must be the same in each case, and when this is so the plane of the grating will be normal to the collimator axis. Let this reading be  $\theta_1$ . Then, since

$$\lambda = b \sin \theta_1$$

as the first order spectrum is under examination, we have

$$b = \frac{\lambda}{\sin \theta_1}.$$

As a check on this, the same line should be examined in the second order spectrum, so that if  $\theta_2$  be the angular deviation,  $b = \frac{2\lambda}{\sin \theta_2}$ .

**SPECIFIC REFRACTIVE CONSTANT.**—If a hollow prism be filled with a liquid, and its refractive index for a given ray ascertained, the specific refractive constant is given by the expression  $\frac{n-1}{d}$ , where  $n$  is the refractive index found and  $d$  is the density of the liquid. This expression may be written

$(n-1)v$ , where  $v$  is the specific volume—that is, the volume occupied by 1 gram of the substance. This ‘constant’ is considerably affected by variations of temperature, and a theoretical expression is more generally employed as follows :

$$\frac{n^2-1}{n^2+2} \cdot \frac{1}{d}, \text{ or } \frac{n^2-1}{n^2+2} \cdot v.$$

This expression is almost independent of temperature, as instanced by the following figures, given by Dr. Walker,\* of water in the liquid and gaseous state at  $10^\circ \text{C.}$  :

	$(n-1)v.$	$\left(\frac{n^2-1}{n^2+2}\right) \cdot v.$
Liquid	·3338	·2061
Gaseous	·3101	·2068

It will be seen that there is a variation of ·0237 when the expression  $(n-1)v$  is used, whilst with the theoretical constant the difference is only ·0007.

The *molecular refractive power* is the product of the above constant into the molecular weight of the liquid ; thus the theoretical molecular refractive power is given by the expression

$$\frac{n^2-1}{n^2+2} \cdot Mv.$$

This expression gives an additive quantity, and in a homologous series the difference between the molecular refractive powers of *adjacent* members of the series is fairly constant. It is possible to obtain the theoretical molecular refractive power, therefore, of elementary substances, such as carbon, hydrogen, oxygen, and so on, and to thus estimate by addition the molecular refractive power of a compound. If  $m$  be the molecular weight of a compound composed of elements

\* ‘Introduction to Physical Chemistry.’



whose atomic weights are  $m_1, m_2, m_3 \dots$ , and  $r$  be the specific refractive constant of the compound, and  $r_1, r_2, r_3 \dots$  the constants of the elements, then

$$mr = m_1r_1 + m_2r_2 + m_3r_3 + \dots$$

The atomic refractive power of an element will vary according to the conditions under which it is combined; thus hydroxyl oxygen and carbonyl oxygen have different refractive powers.

When two liquids are mixed in unknown proportions, the relative quantities of each present can be ascertained if the specific refractive powers of each be known. Thus, if 100 parts of the mixture contain  $x$  parts of one of the constituents, and therefore  $100 - x$  parts of the other, and  $n_1, n_2, n_3$  be the refractive indices, and  $v_1, v_2, v_3$  the specific volumes of the mixture, the first and the second constituents respectively, then

$$(100 - x)(n_2 - 1)v_2 + x(n_3 - 1)v_3 = 100(n_1 - 1)v_1,$$

whence

$$x = 100 \frac{\{(n_1 - 1)v_1 - (n_3 - 1)v_3\}}{\{(n_2 - 1)v_1 - (n_3 - 1)v_3\}}.$$

The *atomic refractions* of some of the elements are given below in Table A, and the molecular refractions of some compounds in Table B, both obtained by the theoretical expression  $\frac{n^2 - 1}{(n^2 + 2)d} \cdot (A \text{ or } M)$ , where  $A$  is the atomic weight and  $M$  the molecular weight.

TABLE A. ATOMIC REFRACTIONS FOR  $\lambda = 6562$ .

Element.	Atomic Weight.	Value of $\frac{A(n^2 - 1)}{d(n^2 + 2)}$ .
Carbon	12	2.48
Hydrogen	1	1.04
Chlorine	35.5	6.02
Nitrogen	14	3.02
Hydroxyl oxygen	16	1.58
Carbonyl oxygen	16	2.34

TABLE B. MOLECULAR REFRACTIONS AT 20° C.

Compound.	Molecular Weight.	Value of $\frac{M(n^2-1)}{d(n^2+2)}$ .
Methyl alcohol	32	8.22
Ethyl alcohol	46	12.78
Propyl alcohol	60	17.34
Butyl alcohol	74	21.90
Benzol	78	25.93
Toluol	92	30.79
Glycerin	94	20.50

It must not be thought that the molecular refractive power is only of interest in the case of organic bodies. *Bender's*\* investigations with solutions of sodium chloride have shown the molecular refraction of NaCl for the D line to be 9.273, whence the atomic refraction of sodium can be found, and is 3.493. The index of refraction of metallic sodium is thereby deduced, and for it

$$\mu_D = 1.23601.$$

There is little doubt that in the near future most extensive applications to general chemistry will be made of work depending on refraction constants.

If a *hollow prism* be filled with a solution of carbon disulphide a continuous spectrum is obtained therewith, the dispersive power of CS<sub>2</sub> being considerable. But if for carbon disulphide we substitute a solution of fuchsin, the green portion of the spectrum will be absorbed, and the red and violet portions transmitted; these will be refracted so that the violet portion lies on the opposite side to the red compared with ordinary dispersion—*i.e.*, the red is refracted *more* than the violet. Such a phenomenon was termed *anomalous dispersion* by Le Roux, who made the discovery with

\* *Ann. Physik*, 1902 (iv.), 8.

iodine vapour in a hollow prism, in 1862. Kundt has since suggested several laws which show the relations between absorption and refraction. The deviation of rays of wave-lengths less than those of an absorption band is greatly increased (above the normal) and largely decreased (below the normal) in the case of rays of greater wave-length. The position of an absorption band in a dye is dependent, according to Kundt, on the refractive index of the medium in which the dye is dissolved, and the absorption band is shifted towards the red end of the spectrum more and more as the refractive index of the solvent is increased.

RESOLVING POWER OF PRISMS AND GRATINGS.—It has been shown that if with a given prism the angular deviation for a line of wave-length  $\lambda_1$  be  $d_1$  and that for a line of wave-length  $\lambda_2$  be  $d_2$ , the dispersion of the prism between these lines is  $d_1 - d_2$ . The dispersive power of a prism may also be expressed in the differential form  $\frac{d\theta}{d\lambda}$ , which expression follows from dividing  $d_1 - d_2$  by  $\lambda_1 - \lambda_2$ . The resolving power of a prism is, briefly stated, the quotient obtained by dividing the mean wave-length of two lines which are just separated by the difference in wave-length between them, or  $\frac{\lambda}{d\lambda}$ . Thus, if a spectroscope with a given prism just separate the green nitrogen lines at 5002·7 and 5005·7, the resolving power ( $r$ ) would be

$$\frac{5005\cdot7 + 5002\cdot7}{2 \times 3},$$

or

$$r = 1668\cdot0.$$

The resolving power of a spectroscope which would just separate the yellow sodium lines would be 982.

*Rayleigh's* fundamental relation that

$$r = -T \cdot \frac{d\mu}{d\lambda}$$

(where  $T$  is the difference in thickness of glass through which the extreme rays of the collimated beam have passed) shows that for a given material the resolving power is *proportional to the length of the prism base*, provided the whole of the first prism face be illuminated by the beam.

The *dispersion* and the *resolving power* are not dependent on one another—*i.e.*, as great dispersion may be obtained with a number of small prisms whose bases aggregate in length to  $\Sigma l$  as with one large prism whose base is  $l$ . But the resolving power of the latter would be the greater.

The *resolving power of a diffraction grating* is given by the product of the number of rulings used in forming the spectrum and the number of order of the spectrum. Thus, with 10,000 rulings a resolving power of 10,000 is obtained with the first order spectrum, of  $n \times 10,000$  with the  $n$ th order spectrum. If the minimum of light in the diffraction image for a line of wave-length  $\lambda$  be coincident with the maximum of light for a line of wave-length  $\lambda_2$ , then it can be shown that the two lines will be resolved. The condition for this is—

$$\frac{\lambda_1}{\lambda_1 - \lambda_2} = mn,$$

where  $n$  = the number of rulings and  $m$  = the number of order of the spectrum. Hence, as  $mn$ —*i.e.*, the resolving power—increases,  $\lambda_1 - \lambda_2$  becomes smaller, and, consequently, lines of smaller difference in wave-length are resolved.

A certain amount of light of all wave-lengths is absorbed by glass; hence the total luminosity of the spectrum will not be as great as the luminosity of the beam which meets the first prism face. Assuming the face to be completely illuminated, then the mean path travelled =  $\frac{b}{2}$ , where  $b$  is the length of the prism base.

Consider a  $60^\circ$  prism, ABC, and two small  $60^\circ$  prisms, DBF and EFC (Fig. 30). The dispersing power of the one large prism is as great as that of the two small ones. DE is the mean path travelled by the beam through ABC, and the

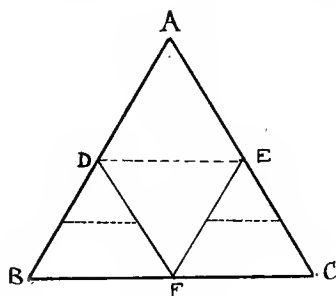


FIG. 30.

sum of the mean paths through DBF, EFC, is obviously equal to DE; hence the absorption is the same whether the one large prism or the two smaller ones be used, the dispersion remaining constant.

## CHAPTER IV

- ✓ The spectroscope in chemical inorganic analysis—Scaling the prism spectroscope—Line spectra—Formation by spirit-lamp, Bunsen burner, electric arc and spark, and by vacuum tubes—Character of the lines.

IF we examine the flame of a Bunsen burner in which some sodium salt is being burnt, we notice at once a bright yellow line in the spectrum, and the eye sees this line—which is really a yellow image of the slit—because the optic nerve is stimulated by light undulations of a certain wave-length. On making the slit of the spectroscope still narrower, the bright yellow line becomes resolved into two lines, whose relative brightnesses are in the ratio of 10 : 7. The wave-lengths of the undulations to which the two lines are due are approximately  $5890 \times 10^{-3}$  centimetres and  $5896 \times 10^{-3}$  centimetres. The term 'tenth-metre' (a ten-millionth of a millimetre) is generally known as the Ångström unit, so that the mean wave-length of the sodium lines is more conveniently expressed as 5893 A.U.

If some thallium salt were burnt in the flames, we should see a bright green line of wave-length 5350.6 A.U., and so on, different metals giving different lines, if a flame in which they are burning be examined.

In order to actually burn the metal, the flame must be sufficiently hot, first, to completely dissociate it from any radicle with which it may be combined; and, second, to vaporize the metal and ignite the metallic vapour. Such flames as given by the spirit-lamp and Bunsen burner are,

therefore, only available in the case of metals which volatilize at a comparatively low temperature. Such metals as sodium, lithium, potassium, thallium, barium, calcium, and strontium, may be recognized from the lines they give when their salts are burnt in a Bunsen flame. But when we come to such metals as iron, cobalt, silver, and so forth, the electric arc or spark is necessary. By burning a substance in a suitable flame, examining the lines in the spectrum produced, and determining the wave-length of those lines, an analysis can be made of that substance. Thus, the wave-lengths of the principal lines in the flame spectra of the metals lithium, sodium, and thallium, are as follows :

Lithium	6708 A.U.
Sodium (mean)	5893 „
Thallium	5350.6 „

Ordinary *spectrum analysis*, therefore, consists in determining the wave-lengths of the bright lines which are seen in the spectrum when the substance under examination is burnt in a suitable manner, and the source of light formed by its burning is examined. This part of the work is restricted to inorganic chemistry, such as general and metallurgical analysis. Organic compounds can be investigated by other spectroscopic methods, which are described in a later chapter.

For the present, then, our work turns upon the *determination of wave-lengths*. The prism spectroscope enables us to find the angular deviation of a line—or, in other words, to find the exact angle which the telescope must make with the collimator in order that a given line may appear in the centre of the field of the eye-piece, as shown by cross-webs or a pointer therein fixed.

We shall now proceed to describe the method of *scaling a spectroscope*—*i.e.*, furnishing a ready means of converting angular deviations (as read on the divided circle) into wave-lengths. To know that the deviation is  $65^{\circ} 14'$  when a

certain yellow line is examined tells us nothing ; but to know that the wave-length of that line is 5790.5 A.U. tells us that it is one of the mercury yellow lines.

The method in common use of scaling the spectroscope is as follows : A number of lines of known wave-length are examined, and the angular deviations corresponding to each are carefully read. Two axes at right angles are then drawn on squared paper, and along one axis are measured wave-lengths, along the other angular deviations. Assuming wave-lengths are abscissæ, the ordinates are drawn for the angular deviations found for the known lines, and the points thus obtained on the squared paper are joined up by a free-hand curve, which curve represents the angular deviations for all rays for the spectroscope in question. It will be obvious that, if the dispersion be caused by a grating placed normally to the collimator, the curve will be a straight line, as then wave-lengths are directly proportional to the angular deviations.

In order to draw the curve or scales accurately, as many lines of known wave-length as possible should be measured. The scaling of a given spectroscope was done by means of the following lines :

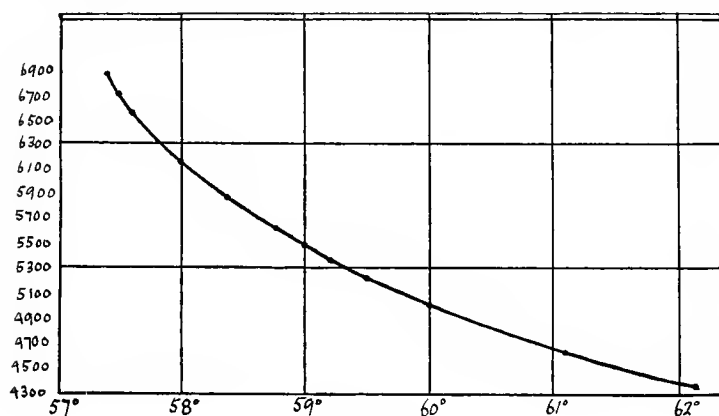


FIG. 31.



EXTRA DENSE FLINT PRISM, IN MINIMUM DEVIATION  
FOR  $\lambda = 5893$  A.U.

Line.	Source.	Angular Deviation.	Wave-length.
Mercury violet	Hg vacuum tube	62° 7'	4358·6
Barium violet	Ba in spark	61° 20'	4554·0
Nitrogen violet	Air spark	61° 5'	4630·0
Hydrogen blue	H vacuum tube	60° 21' 30"	4861·5
Nitrogen green	Air spark	59° 56'	5002·7
"	"	59° 55' 30"	5005·7
Copper green	Cu in spark	59° 30'	5218·4
Lead green	Pb "	59° 13'	5373·6
Mercury green	Hg vacuum tube	59° 0'	5461·0
Lead green	Pb in spark	58° 46'	5607·3
Mercury yellow	Hg vacuum tube	58° 31'	5769·5
"	"	58° 29' 30"	5790·5
Mean sodium	Na in Bunsen burner	58° 22'	5893·2
Lithium orange	Li in spark	58° 5'	6103·8
Mercury orange	Hg vacuum tube	58° 0' 30"	6152·3
Hydrogen red	H vacuum tube	57° 36'	6563·0
Lithium red	Li in Bunsen burner	57° 30'	6708·2
$\beta$	Sunlight	57° 22'	6867·5

These eighteen lines are well distributed throughout the spectrum, are well defined, and should prove sufficient to give a reliable curve for reference. Plotted out in the way already indicated, they provide the curve shown in Fig. 31, which may be calibrated by means of other lines of known wave-lengths. The dispersion of a prism being abnormal, the curve has a very decided shape, but a much flatter curve may be obtained if, instead of using wave-lengths for our measurements, we use oscillation frequencies—*i.e.*, the reciprocals of the wave-lengths. The wave-length curve is, however, the more useful at the present time.

The deviations for the lines may either be read with the prism placed in the position of minimum deviation for each, or it may be fixed at minimum deviation for some mean ray, such as the mercury green. If the in-

strument be a two-prism spectroscope the prisms should be kept fixed always. But with one large prism it will be found sufficiently accurate for general work to keep it in one fixed position, as if it be altered for every ray examined great precision is needed, both in the instrument and in the observer; and, moreover, such a degree of precision is only required for special work, as will be seen later.

When using a *diffraction grating* normal to the collimator great precision is obtained by reading the angular deviation  $\theta_1$  for a given line in the first order spectrum, and then still further turning the telescope until it is seen in the second spectrum, when the new angular deviation  $\theta_2$  should be equal to  $2\theta_1$ ; if it be not quite equal, then  $\frac{\theta_1 + \theta_2}{3}$  will give an average of the two readings. Or the line may be observed first one side and then the other side of the collimator axis, when the angular deviations should be exactly equal, or if not, the average  $\frac{\theta_1 + \theta_2}{2}$  may be taken.

When using the prism spectroscope a line should be examined at least twice, and the angular deviations determined each time; these should, of course, agree, but if a slight difference is found, either a third reading should be taken or an average of the two already made.

*Line spectra*, as produced by a flame, the arc or spark, may be divided into four classes:

1. Sharply defined on both sides.
2. Diffused on the 'violet' side, sharply defined on the 'red' side.
3. Diffused on the red side, sharply defined on the violet side.
4. Diffused on both sides.

Many lines which at first appear single become resolved into two or more lines under more critical examination—*i.e.*, with narrower slit or with an instrument of higher resolving power.

Well-defined lines should be chosen, if possible, for wave-length determination in making an analysis of an inorganic substance; each line should be made as narrow as possible by using the slit very narrow, and the line being seen clearly passing through the X of the spider-webs in the eye-piece, the angular deviation for that line is read.

The position of a line due to a metal does not depend on the salt of the metal used—the chloride, nitrate or sulphate, etc. The number of lines given by any metal depends largely on the temperature of the flame, but temperature does not affect the positions of lines.

If the spectrum of white light be examined it is seen to be continuous. If now a sodium flame be placed between the white light and the slit, two *dark lines*, or *absorption bands*, will be seen in the yellow region, and the wave-lengths of the two coloured rays thus absorbed may be found to be 5890 and 5896 A.U. If now the *white light* be taken away, the two yellow *bright* sodium lines will be seen to occupy the positions just occupied by the two dark lines. This phenomenon shows us that the yellow sodium flame, whilst itself emitting light of wave-lengths  $w_1, w_2$ , etc., has the power of absorbing light of wave-lengths  $w_1, w_2$ , etc., when light containing rays of those wave-lengths is passed through it.

A luminous body may, therefore, be said to emit rays of light of certain wave-lengths under the necessary conditions; it also exerts an abortive power for the same rays. According to Kirschhoff, the relation between the powers of emission and absorption for rays of the same

wave-length is constant for all bodies at the same temperature.

The sun may be regarded as consisting of a white-hot nucleus, surrounded by gases and vapours. The latter absorb certain rays of the white light emitted by the sun itself, and hence in the spectrum of sunlight are seen numerous dark lines—the *Fraunhofer lines* of the solar spectrum. It is from examinations of these lines that the constitution of the sun and many stars has been partially determined.

The chief Fraunhofer lines are as follows:

A (deep red)	Wave-length	7594
B „	„	6867
C (bright red)	„	6563
D <sub>1</sub> (orange-yellow) -	„	5896
D <sub>2</sub> „	„	5890
D <sub>3</sub> (yellow) -	„	5876
b <sub>1</sub> (green) - -	„	5184
b <sub>2</sub> „ -	„	5173
F (blue) - -	„	4861
G (violet)	„	4308
H „ -	„	<del>3967</del> 3969
K „	„	3934

Dark, or reversed, lines sometimes appear in arc spectra; thus in the iron arc the lines  $\lambda = 4384$  A.U. and  $\lambda = 4294$  A.U. are sometimes found reversed.

It will be noticed in spectra obtained with a prism spectro-scope that many of the *lines* are *curved*, their convex sides being towards the red end. This is due to the fact that only the rays from the *centre* of the slit are rendered absolutely parallel by the collimator. The centre of the line should be used for purposes of measurement.

## EXAMINATION OF METALLIC SALTS WITH SPIRIT-LAMP.

The *spirit-lamp*, as already intimated, is only useful in a few instances. A good method is to invert the lamp and dab the wick into the substance; when lighted, the flame will be well coloured, and the lines clearly seen in the spectroscope.

The substance may be introduced into the hottest part of the flame by means of a platinum or iron spiral which has been dipped into it. The wire may be fastened into a glass-tube handle, or may be attached to the upright of a retort stand. Where a continuous sodium flame is required for monochromatic light purposes, as in refractive index determinations, etc., a lump of rock-salt may be fastened with a coil of stout iron wire, the wire fixed to a retort stand, and the coil and salt placed in the edge of the flame.

## EXAMINATION WITH BUNSEN BURNER.

The platinum or iron wire may be used as before to introduce the substance into the flame. A wire which has once been used should be cleansed with hydrochloric acid before it is used a second time.

A special form of Bunsen burner for producing a sodium or other flame for monochromatic light work and spectrum examination is shown in Fig. 32. The small cup for holding the substance under examination can be turned out of the flame when desired, and removed for cleaning, recharging, etc. The height of the flame may be regulated by means of the screw S in order to suit the spectroscope.

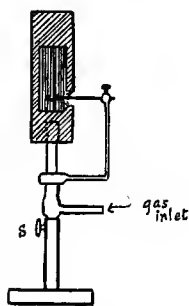


FIG. 32.

A new Bunsen burner attachment has been brought out recently by Carl Zeiss, a sketch of which is seen in Fig. 33. The attachment consists of a screen, KK, with a central rectangular aperture, L, through which the chief portion of the flame is observed. The casting, A, carries this diaphragm

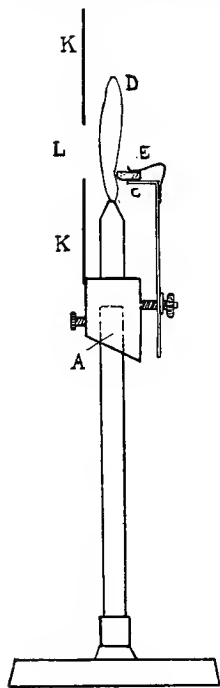


FIG. 33.

screen, and also a flat burner, C, which produces a square flame. E is an adjustable clip, into which is fixed a piece of pumice-stone, measuring about  $4 \times 1 \times 0.5$  centimetres, saturated with the salt. It is best to adjust the pumice-stone so that it merely touches and tinges the flame. If it be too deeply inserted, the flame will be cooled down too much. The flickering margins of the flame are cut off by the diaphragm.

A method of continuously supplying the flame with the substance is to have a revolving tilted asbestos disc, the lower edge of which dips into a strong solution of the chemical matter, the upper edge being in the bottom of the Bunsen flame. This is a modification of the method devised by Eder and Valenta, in which two metal discs were used, a ring of platinum gauze being fixed between their edges. The axle of the wheel made an angle of  $45^\circ$  with the vertical, and was actuated by a clockwork motor.

Lime cylinders may also be used, heated by oxy-hydrogen, or oxygen and gas, the limes being previously brushed over with the chemical solution, and allowed to dry before use. The investigations of Hartley\* into the banded

\* Phil. Trans., 185, 1894.

spectra produced by the oxy-hydrogen flame are worthy of study.

#### EXAMINATION WITH THE ELECTRIC ARC.

The *electric arc* is a very convenient source of heat for the production of spectra, owing to its high temperature; and in the case of such salts as those of sodium, potassium, etc., many more lines are to be found when the arc is used to burn them. The arc flame itself gives a great number of lines, partly due to its gaseous constituents, and partly due to the impurities present in the carbon rods; thus, the sodium yellow lines, the calcium lines at 3934 and 3967, several aluminium lines, *b*, and others, are to be seen, and several iron lines as well.

It is a great advantage to eliminate these as far as possible; and although it can never be done completely, great purity may be obtained by soaking the rods for a week each in the following: aqua regia, nitric acid, fluoric acid, hydrochloric acid, potassium hydroxide solution, distilled water (several changes).

The arc-lamp most suitable for spectroscopic work is the hand-feed pattern, in which the positions of the carbons are controlled by a simple rackwork motion. Narrow carbon rods, of about 1 centimetre diameter, will be found amply large, and a current of 3 to 6 ampères will be required on a 100-volt circuit.

In order to examine a substance by means of the arc, the carbon rods may be drilled with a central hole, and these holes packed with the substance, or the crater of the positive rod may be packed with it. A more convenient way is to boil a rod for some time in a concentrated solution of the substance, allowing the solution to become quite syrupy, so that an excess of the metallic salt crystallizes on the surface. These crystals must be scraped off, or the flame will flicker.

Where much work is to be done with one metal, a rod of it may be substituted for the carbon rod, but this is only possible in the cases of metals of very high melting-point, many metals melting away under the heat of the arc.

Where a brief examination only is required, it will suffice to brush the poles over with a solution of the substance. But it will be noticed that, whilst this procedure will readily give bright lines with salts of some metals, it will not do so with others. Thus, a trace of weak lithium chloride solution will give the lines at 4602, 6104, and 6708 readily; but with a zinc salt the 'coring' or packing methods are necessary, a weak solution applied with a brush being entirely unsatisfactory.

#### EXAMINATION WITH ELECTRIC SPARK.

The electric spark obtained from an induction or Rhumcorff coil may be utilized for the production of spectra. In this case we are dependent on an exceedingly high voltage and infinitesimal current, instead of a moderate voltage and large current, as in the case of the electric arc.

A good deal depends on the size of the coil used. It must be fairly large in order to give complete satisfaction; and after protracted trials with various coils, capable of giving sparks from 1 to 12 inches in length, the writer has elected to use a 6-inch spark coil, of a type intended to give a tolerably heavy current for X-ray and general laboratory work. A 2-inch spark coil is usually looked upon as the minimum size suitable for practical work; but the advantage of a powerful coil will be appreciated by those who have undertaken much spark work with the spectroscope.

The heat of the spark is greatly increased and the discharge rendered oscillatory by putting one or more Leyden jars in parallel with the secondary coil. The general arrange-



ment is seen in diagram form in Fig. 34. The primary terminals, P, P', of the coil are connected with the two terminals of an accumulator or primary battery, B. The secondary terminals, S, S', are connected by wire to the inner and outer coatings of a Leyden jar, L, and thence, in parallel, with the terminals of the sparking apparatus, T, T', which apparatus, together with the Leyden jar, have, for the sake of clearness, been represented in elevation.

As a fairly large current consumption is required, it will be found a great convenience to have a good accumulator of the necessary voltage which will stand a heavy discharge, such

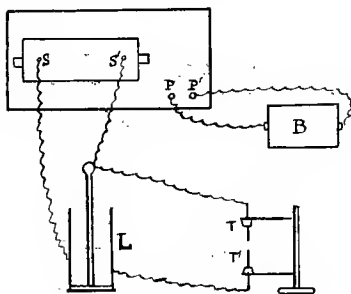


FIG. 34.

as 5 to 6 ampères. Primary batteries are a nuisance and, as a rule, unsatisfactory; but if they must be used, Bunsen cells are really preferable to anything else.

The form of *interrupter* (contact-breaker) is one of vital importance. Large coils can always be provided with a mercury-motor interrupter or an electrolytic break, but these require from 24 to 50 volts to work them satisfactorily. They are to be recommended whenever current from the mains is available. The ordinary form of platinum interrupter, which is seen in Fig. 35, has an objectionable tendency to stick, which endangers the insulation of the coil and ruins accumulators, unless a fuse be employed in

the primary circuit. Here E is the end of the iron core, H the hammer, P, P' the platinum contacts, and S the regulating screw, usually fitted with a locking arrangement, L. T is the tension screw, by turning which in one direction the hammer spring can be drawn towards the pillar Q, and more current will thus be required to work the coil; hence a thicker and hotter spark. The contacts P and P' often stick together, and the current must then be at once switched off.

In order to get the best results, S should be turned,

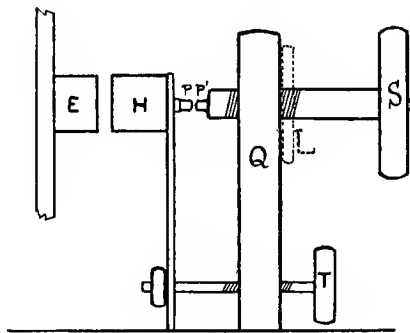


FIG. 35.

T being quite loose—*i.e.*, there being no tension—until P and P' almost touch. The current is then switched on, and the tension screw turned until the necessary spark is obtained. But to get the *longest* spark, S should be turned until it pushes the hammer within  $\frac{1}{32}$  inch of the core end, E. The coil is then started, and the tension screw regulated as desired.

The '*Vril*' interrupter, made by Messrs. Watson and Sons,\* is one which never sticks, and the coil can be run for a couple of hours without attention if desired. The action is

\* 313, High Holborn, London, W.C.

seen in Fig. 36. The hammer contact,  $P'$ , is attached to a separate spring,  $K$ . When  $H$  is attracted to  $E$ , the screw  $W$  presses against the top of  $K$ , and draws  $K$  with it, thus separating  $P$  from  $P'$ . By altering  $W$ , the distance  $H$  travels before  $K$  is touched can be varied; and by making the distance between  $W$  and  $K$  great, it will be seen that  $P$  and  $P'$  are in contact a considerable time before separation. Thorough saturation of the core is thereby accomplished, and magnificent results obtained. In fact, we cannot too highly emphasize the efficiency and convenience of this

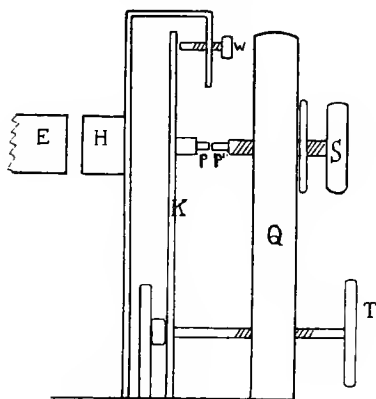


FIG. 36.

interrupter.\* When only a short spark is required, it may be treated precisely as an ordinary form of interrupter.

The introduction of the substance into the spark may be accomplished in different ways, and depends largely on whether it be of a solid or liquid character. One simple apparatus which may be used in the case of liquids is seen in

\* The Leyden jar capacity varies with different forms of interrupter, and the number and size required has always to be found by experiment.

Fig. 37. A glass test-tube is provided with a cork fitted with a tube, into which is sealed a platinum wire, the wire projecting a few millimetres from the end of the tube. A short platinum wire is fused into the bottom of the tube, and a small capillary cone is fitted loosely over it as



shown, so that when a little of the liquid is placed at the bottom of the tube it rises to the top of the capillary. The coil is then connected with T, T', and a spark passes between the platinum point and the solution. If desired, a delivery and exit tube can be fitted into the cork, so that a stream of hydrogen or other gas can be passed through the apparatus, and the spark examined in the gas.

A simple apparatus in use by the writer will be seen in Fig. 38. Here a piece of glass-tubing of about 3 or 4 millimetres bore is fixed to a wooden upright at an angle to the upright. A long platinum wire emerges from the lower end, which has been drawn out to a point and broken, so that the bore is about 1.5 millimetres. A finely pointed pure carbon cone or another platinum

FIG. 37.

wire is fixed underneath the upper wire, and, whilst the spark is passing between the two, the liquid to be examined may be introduced into the mouth of the tube, and it very slowly drips out of the end and descends the wire, where it instantly colours the spark.

Where work with a known metal is to be done, it is, of course, best to use wires or pointed cones of the metal. Purified charcoal or carbon cones may also be boiled up in a solution of a salt to be examined, and used as the points between which the spark passes; the spectrum is generally brighter when the spark is moistened with water or hydrochloric acid. The non-metallic elements, or the radicles, of

a salt do not as a rule affect the spectrum; and, according to Hartley, solutions of the metallic chlorides give spectra the lines of which are precisely the same as those of the metals themselves.

The nature of the lines in spark spectra deserves consideration. With a spark-gap of about an inch, and one or two Leyden jars in the secondary circuit, the principal lines in the spectrum will be air lines, due to nitrogen, oxygen, etc. Thus, the 'air' lines (due to N) at  $\lambda = 5002.7$  and  $\lambda = 5005.7$  A.U. are always very distinctly seen, amongst others.

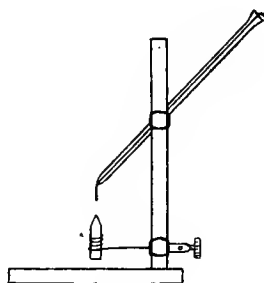


FIG. 38.

If a lens be used to cast an image of the spark on the slit of the spectroscope, it may be seen that all the lines are not of the same length. Some lines will, for example, be seen most distinctly near the electrodes, and do not extend across the spark-gap; the air lines extend across the spark-gap, and may be brightest in the centre of the field. When water is used to moisten the electrodes, the shorter lines are lengthened.

The effect of *self-induction* has been largely studied by Hemsalech, Schuster, and others. A self-induction coil, made by winding wire in the way used for a straight electromagnet, if placed in series with the spark-gap in the secondary circuit, will have the effect of reducing the number of air lines in the spectrum, and of narrowing the metallic lines. Schenck found, with the cadmium spark spectrum, one set of lines which only extended a short way across the spark-gap disappeared on the self-induction coil being used; another set included the lines which were weak in the arc spectrum of cadmium, or did not appear in it at all, and a third set which were found also in the arc.

## VACUUM-TUBE SPECTRA.

When a gas is in a rarefied condition, and the spark from an induction coil is passed through it, a line or band spectrum is produced. The spectra of many elementary gases, when examined by means of the vacuum tube, are complicated, and what appear at first sight to be bands prove in reality to be masses of fine lines packed closely together. The nature of the spectrum depends on the degree of vacuum in the tube, and the intensity of the spark has considerable influence on its brilliance. The spectrum of hydrogen is more or less continuous at a pressure of half an atmosphere, whilst with very small pressure at least twenty-two principal lines are to be found.

The alteration of the spectrum with alteration of pressure may be accounted for, according to Watson,\* in the following way: When a gas is under low pressure, the mean free path of the molecules is great, so that the interval between the successive impacts of a molecule with another is great. During the impact the atoms will be set into various kinds of forced vibrations, but all except those which correspond to the natural vibrations of the atoms will rapidly die out, and hence the atoms will be vibrating in their own natural period for the greater part. If the light emitted by a glowing gas is due to the vibrations of the atoms, at low pressures the gas will give out light of certain definite wave-length, corresponding to the natural periods of the atoms. With increased pressure the mean free path of the molecules becomes less and the impacts more frequent. The forced vibrations, which are of almost equal period to the natural period, will begin to take effect and the bands will widen out. Eventually, therefore, with increase of pressure, a continuous spectrum may be produced.

\* 'A Text-Book of Physics.'

Vacuum tubes are very convenient for scaling spectroscopes or spectrographs, or for investigations into the relationships between lines (see Chapter IX.), and so forth. They are, however, of little use for analytical work, except in the case of the examination of an unknown gas.

The usual form of tube is seen in Fig. 39 (a), the capillary portion being placed in front of the slit. Fig. 39 (b) shows a laboratory tube which can be filled with an unknown gas, and then exhausted by means of a mercury pump.

Mercury and hydrogen lines are apt to occur in all vacuum tubes, the former owing to the use of the mercury pump, the latter owing to occlusion of hydrogen in the (aluminium) electrodes.

The 'bands' of fine lines, such as are found in the nitrogen spectrum, culminate in a bright 'head,' and the intensity of the lines diminish from the head towards the opposite side.

It must be borne in mind that it is practically impossible to form any *quantitative* idea as to the amount of one metal present among others. Sodium, for example, gives the two yellow lines with such remarkable readiness that the minutest trace is noticeable; in fact, it is often very difficult indeed to get rid of the sodium lines.

It may not be irrelevant to mention here some recent work

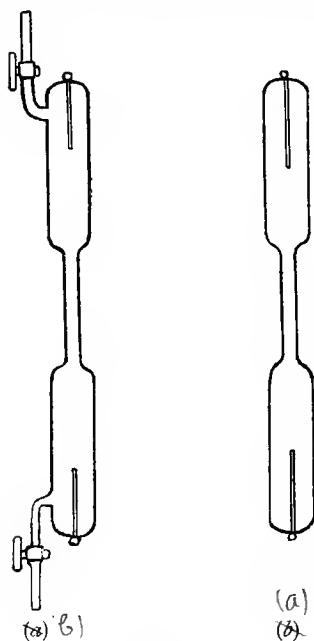


FIG. 39.

done on the purification of selenion by R. Threlfall.\* The selenion was separated by the fractional sublimation of the oxides. The sublimate obtained contained less than  $\frac{1}{10}$  per cent. of tellurium, and 'probably less than  $\frac{1}{40}$  per cent.' A thorough investigation showed that tellurium cannot be detected by spectroscopic analysis when in the presence of selenion in quantity.

The quantity of an impurity detected by the spectroscope might appear greater or less according to the radicle with which the metal was associated.

\* Proc. Royal Soc., 1907.



## CHAPTER V

Continuous spectra—Banded spectra—Illuminants—Colour—Complementary colours—Fluorescence—Calorescence—Chemical energy and heat energy : their distribution in the spectrum.

IN the last chapter line spectra were more especially considered, and methods of inorganic analysis by the wave-length determination of the lines described. When a body, such as a metal, is heated, it becomes red-hot with the rise of temperature, and emits chiefly rays of large wave-length. As the temperature still further rises the body becomes *incandescent*, and, if its illumination be examined, a continuous spectrum will be observed—that is to say, an uninterrupted band of light of all wave-lengths within visible limits. The relative intensity of the different regions of the spectrum, however, varies with different sources of illumination. The power of the arc light depends on the incandescence of the poles. The incandescent gas light is dependent for its illumination upon the incandescence of the ‘ash’ contained in the mantle, which is caused by the heat of the mixture of gas and air which is burning around it. The light given by a candle flame is due chiefly to particles of incandescent carbon, which are obtained from the wax drawn up by the wick.

A *comparison of the spectra* of various illuminants may be made in one of two ways : either the spectrum may be examined in contact with a standard or known spectrum by means of a comparison prism fitted to the slit, and the

intensities or luminosities of contiguous narrow regions compared; or photographs may be taken of the various illuminants by means of a spectrograph, and the densities of contiguous narrow regions in the negatives read by means of a photometer (see p. 107), and these densities compared.

A photograph in natural colours\* of the spectrum of incandescent gas light is seen in the frontispiece, and though



Incandescent Electric-light.



Arc-light.



Daylight.

FIG. 40.

the limitations of the half-tone process (by which it has been reproduced) have rather detracted from its correctness, it nevertheless gives a very fair idea of the spectrum as seen in the grating spectroscope.

The three photographs of spectra shown in Fig. 40 give some idea of the differences in the *distribution of colour* in daylight, arc light, and the light from a 16-candle-power electric glow-lamp. The latter gives a great deal more red,

\* Full details of the methods adopted will be found in a paper by the author, communicated to the Royal Photographic Society, January, 1905.

compared with the blue-violet, when worked at a rather lower voltage than the normal, whilst a 100-volt lamp, worked at 120 volts, would give a very large percentage of violet and blue, owing to the greater heat applied to the filament and the greater degree of incandescence. The dark Fraunhofer lines are seen in the daylight spectrum, which is not, therefore, strictly continuous.

In order to compare two illuminants by means of spectro-photography, several photographs should be taken with each light source, and all the photographs developed together under similar conditions. Some spectral region should be selected in which the intensity of the illumination is to be constant. If the opacities in two photographic negatives of the two illuminants are equal between the limits  $\lambda=4000$  and  $\lambda=4100$  A.U., the opacities between all other limits can be compared. Thus, if the opacities between  $\lambda=5800$  and  $\lambda=5900$  A.U. be ascertained and found to have the ratio  $x : x+a$ , obviously the latter illuminant will possess more yellowish-green (compared with the blue at  $\lambda=4000/4100$ ) than the other.

The unevenness in the colour sensitiveness of the plates used must, of course, receive consideration when taking photographs of continuous spectra.

The *spectro-photometer* provides a means of comparing two illuminants in the following manner: The spectrum in question and a standard spectrum are seen one above the other in the eye-piece of the telescope, which is provided with shutters to cut off all but a narrow region, and the intensity or brightness of any region of one spectrum can be reduced by an arrangement of crossed Nicol prisms, and the 'extinction coefficient' determined.

A Nicol prism which polarizes the light perpendicularly is placed so that the beam of standard light passes through it, and it then passes through the second Nicol prism before

being brought to a focus by the telescope, this Nicol polarizing in a plane perpendicular to the first. The rotation of the second Nicol is read off by a vernier, and the extinction coefficient thus obtained.

If contiguous narrow regions of the spectrum be taken, the relative intensities of the upper and lower spectral portions can be compared. The sources of illumination should, of course, be equally bright for one selected region, and all the other regions thus compared. Plaster of Paris discs are provided, by means of which light can be reflected into the slit.

It is worthy of mention that the spectro-photometer, which depends on the crossed Nicol principle for extinguishing the luminosities in one of the spectra compared, is not looked upon by all scientists with equal favour, and one form of instrument in which a wedge of grey glass is used as the extinguishing apparatus is likely to be perfected before very long.

The subject of colour has been mentioned already in an earlier chapter, but we shall briefly refer to it again on the present occasion, as the explanation of *complementary colours* and absorption bands will become necessary in subsequent considerations.

The spectrum, as seen by the eye, consists of innumerable images of the slit of the spectroscope, which form an apparently continuous band. A certain green ray in the spectrum is *pure green*—*i.e.*, the eye is entered by light-waves of a certain frequency. But it is possible, by mixing pure 'blue' and pure 'yellow,' to form 'green'—a compound colour which may be indistinguishable from a pure 'green.' This is explained satisfactorily by the Young-Helmholtz theory of colour vision.

If the continuous spectrum of some white illuminant be examined, and a piece of red glass be then interposed

between the slit of the spectroscope and the source of light, a red band only will be seen; this is, of course, because the red glass absorbs light of all colours except red. If, in Fig. 41, A be the portion of the spectrum absorbed and T the portion transmitted, and the rays of all wave-lengths included in A and T respectively recombined on a screen, two colours would be formed side by side, the red, T, and a green produced by the violet, blue, green, and yellow rays in A. These two colours would be *complementary*, and would, if reunited, form white light; but if two glasses were obtained, one transmitting A and absorbing T, the other transmitting T and absorbing A, and these were both held in front of the eye, no light would be seen, as what rays penetrated one glass would be absorbed by the other. Hence,



FIG. 41.

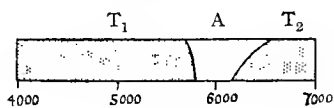


FIG. 42.

light of complementary colours forms white light if recombined, whilst glasses complementary in colour do not allow any light to pass through if held together. If a deep yellow piece of paper be looked at through a deep violet piece of glass it will appear black, and so on.

A piece of violet glass will usually transmit some such portions of the spectrum as  $T_1$  and  $T_2$ , absorbing a green-yellow region A. If  $T_1$  and  $T_2$  were combined, they would give a compound colour of a mauve or purple appearance, and this colour would be complementary to A. A very deep solution of a dye may pass only the red region of the spectrum—at any rate, visually—but on being diluted it will transmit the violet as well, and its appearance will therefore be altered. Thus, a deep solution of some of the *fluorescein derivatives* may look almost vermilion, whilst when diluted

they will appear to be rather of a crimson or carmine colour.

If the light reflected from the surface of a piece of *red* paper be examined by means of the spectroscope, it will be seen to contain only the red portion of the spectrum, or perhaps the red and orange portions. The paper is red because the *pigment* it contains absorbs all except the less refrangible rays of light. The light which meets the surface of the paper enters some appreciable distance into it before it is reflected, and the deeper it enters into the pigment, the more absorption of light of colour complementary to that of the pigment takes place. The colour as seen by the eye is, therefore, the resultant of several component colours, slightly varying from white light reflected from the absolute surface to deep red as reflected from an under layer of the pigment after the fullest absorption has taken place. The amount of white light reflected will depend on the quality of the surface, a shining surface reflecting more than a dull surface. This reflection of a *proportion of white light* from a coloured surface accounts for the effect which red and yellow objects will produce on a photographic plate in the camera, although the plate is known to be practically insensitive to yellow and red rays.

The colour of various chemical compounds has doubtless some connexion with their molecular arrangement. The absorptions of solutions of metallic salts will be discussed in a later chapter, and it will suffice to say here that certain metals are far more active, as far as the coloration of their salts are concerned, than others. Thus iron, nickel, and cobalt give rise to strongly coloured compounds, whilst aluminium, magnesium, potassium, etc., form white compounds under ordinary circumstances.

*Fluorescence* is a phenomenon which deserves some attention from the spectroscopist. According to Stark, the mere

absorption of light in a band spectrum probably produces fluorescence. The wave-lengths of the light in the fluorescent colour are longer than those of the absorption band. Thus a quinine salt fluoresces pale blue, whilst it absorbs a portion of the ultra-violet. It has also been concluded that in the case of fluorescence the light does not enter the solution, but is reflected from the surface, and the wave-length changed during reflection.

The *X rays*, whose wave-length is extremely short—very much less than that in the ultra-violet—produce fluorescence in many inorganic chemicals, such as calcium tungstate, barium platinocyanide, and so on. It is also interesting to note that the fluorescence from an X-ray tube is caused merely by the impact of certain rays upon the glass surface, the fluorescence being bright apple green, or *blue*, according to the kind of glass used in the manufacture of the tube. Recent spectroscopic investigations have shown that the fluorescent rays contain certain spectrum lines, due to the metal of which the *anticathode* is composed; this is only to be expected, since the ionizing power of the rays is so great.

Fluorescence, as observed in solutions of dyes and other substances, does not occur if the solutions be examined in light of certain wave-lengths. Thus a solution of *quinine* does not fluoresce if illuminated by red light, whilst it does fluoresce when examined in violet and ultra-violet light.

The visual examination of the ultra-violet end of the spectrum has been made possible by the ingenious device of Professor Liveing, who suggested the use of an *eye-piece* containing a substance which fluoresces *visible* rays when acted on by invisible ultra-violet rays. A Liveing eye-piece is, therefore, essential to the visual study of ultra-violet lines.

When a substance is capable of absorbing light rays of a certain wave-length, and of emitting them as rays of less

wave-length, it is said to *caloresce*, but our knowledge of *calorescence* at the time is limited.

*Phosphorescence* may be described as a kind of continuous fluorescence, for if a phosphorescent substance receives light, and absorbs it, it emits light of certain wave-lengths, which emission continues after the illuminating source is removed. In the case of the *phosphorescent bacteria*, the emission of light is due to energy transformed by the organisms themselves. The phosphorescence seen in the sea is caused by light-producing infusoria, bacteria, etc., and the latter are chiefly motile bacilli or vibrios. Access to oxygen is absolutely essential to the bacteria, otherwise they do not phosphoresce. The light they produce is, therefore, caused by the surplus energy of respiration. The rays given off by *Bacillus phosphorescens*, *Bacillus luminosus*, etc., are chiefly bluish, but vary between D and G.

A micro-organism test for oxygen has resulted from the spectroscopic experiments of Engelmann: bacteria essentially aerobic were placed in water containing green algal filaments,\* and illuminated by the projection of a spectrum caused by an arrangement of prisms in the sub-stage of the microscope. The aerobic bacteria crowd round the filaments lying between the Fraunhofer lines B and C, and those about the F line, as these are the regions in which most oxygen is produced by the algal matter. As Fischer points out, the absorption spectrum of chlorophyll shows that the regions at B, C, and F are most strongly absorbed, and these are the spectral regions which effect most readily the liberation of oxygen from carbon dioxide.

When we turn our attention to other *chemical*—i.e., less physiological—effects of the spectrum, it is at once found that the violet and ultra-violet regions are most active. As early as 1783 Favre and Silbermann utilized the action of

\* Fischer, 'The Structure and Functions of Bacteria.'



light to make a comparison of the sun's illumination at different times of the day, it having been observed that the spectrum constantly varied. In Fig. 43 will be found the curves they obtained by plotting against wave-lengths the quantities of hydrogen and chlorine which combined in a given time in a series of inverted test-tubes containing a mixture of these two gases, the series of tubes being illuminated by a powerful spectrum. It is, of course, well known that hydrogen and chlorine combine rapidly to form hydrochloric acid in light, but the rate of combination varies with light of different wave-lengths. Favre and Silbermann found that the

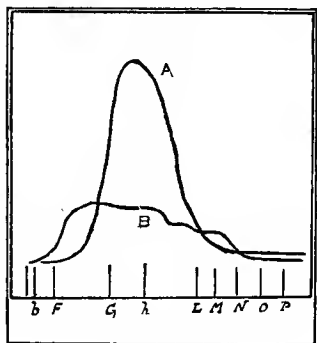


FIG. 43.

water rose in the tubes—*i.e.*, the combination took place—most rapidly in the regions around H and I. The curve A shows the chemical effect of sunlight at midday, whilst B represents the action at evening, with a cloudy sky. The reason the action is so small in the violet region in curve B is simply because the evening atmosphere, etc., acts as a light filter and absorbs much of the more refrangible rays.

The *chemical energy* of the spectrum, then, lies chiefly in the ultra-violet, violet and blue. The two curves given in Fig. 44 show (1) the reducing power of light on gelatino-silver chloride, and (2) the developable effect on gelatino-silver bromide.\*

Solutions of cupric, ferric, uranyl, chromic and other salts are reduced by light; ferric salts become ferrous, and so on. The sensitiveness of molybdenum, tungsten, and other salts is discussed by the author elsewhere.† Although different

\* Eder.

† *Photographic Journal*.

inorganic salts may be affected most by—*i.e.*, show maximum sensitiveness to—different portions of the spectrum, these portions are practically always in or near the blue-violet region.

As regards the heating effect of different rays, a measurement can be made by means of the *bolometer*, an instrument capable of recording extremely small changes of temperature. A dead-black narrow body, illuminated by light of various wave-lengths, will absorb that light under all circumstances; it has been possible, by placing such an arrangement in different portions of the spectrum, to measure their relative

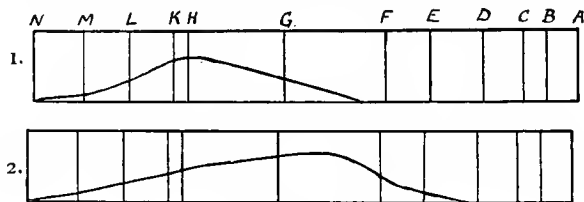


FIG. 44.

heating effects. Accurate bolometers have enabled the *infra-red* solar spectrum to be mapped, a 'bright line' being regarded as present wherever a rise of temperature is observed during the shifting of the bolometer along the spectrum.

Owing to the absorption of heat by various media, a *rock-salt prism* of low heat-absorbing power is used. The heat energy of the spectrum is comparatively small in the violet, blue and green regions, the red and infra-red having far greater effect.

The physiological energy of the spectrum, or the visual brightness of light of different wave-lengths, has been ably discussed by Abney, König, Vierordt, and others. The maximum brightness to the eye lies in the yellow-green region, and the luminosity tapers off gradually towards the red and blue sides.

## CHAPTER VI

Spectro-photography—Forms of photo attachments—The construction of a simple laboratory spectrograph—Resolution and the grain of sensitive plates—Scaling the spectrograph—Photographic methods of wave-length determination—The micro-reader.

AN arrangement by means of which the spectrum or any portion of it can be photographed is termed a spectrograph, and the uses of spectrographs both in commercial and general scientific work are daily becoming more numerous. Photography affords the most accurate means of determining the wave-length of an unknown line when a prism spectro-scope is in use, and the photographic method of wave-length determination will receive full consideration in the present chapter. Other applications of the *spectrograph* are to the investigation of absorption bands in organic substances, the comparison of sources of illumination, the preparation and adaptation to plates of light filters for photo-micrography, orthochromatic and three-colour photography, etc.

The simplest form of *photo attachment* is a small wooden box which can be fitted to the telescope arm of a spectro-scope. Such an attachment is seen in diagram form in Fig. 45. Here T is a short brass tube with the telescope objective at O; the tube is fixed by a flange to the box, which has a short bellows, B, connecting it to the plate-holder or dark-slide MN, the bellows enabling a swinging movement of MN possible, which is necessary to get sharp definition at both ends of the spectrum, owing to the abnormal dispersion of a prism. A brass-slotted strut, S,

is provided to clamp the two portions of the camera when the inclination of MN to OT has been found by focussing or some other means.

A spectrograph made entirely for photographic work is shown in Fig. 46. The telescopic camera revolves about a centre which is the centre of the prism table, and a quartz prism is provided in this case, so that the ultra-violet region of the

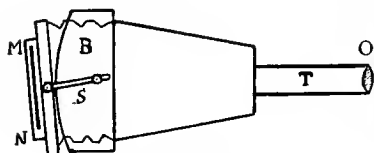


FIG. 45.

spectrum may be photographed; quartz lenses are therefore used for the collimator and objective. The dark-slide is movable in a direction perpendicular to the length of the spectrum, so that several photographs can be taken on one plate, the slide being moved between each exposure.

It is essential that any form of photo attachment be exceedingly rigid, and that the dark-slide be provided with some means of keeping the plate very tightly in position—*i.e.*, to prevent any play.

The length of the spectrum on the plate will depend on the size of the instrument and the dispersion of the prism. With the same instrument we can get a longer spectrum by using a telescope lens of longer focus; thus a 12-inch focus lens will give a much shorter spectrum than an 18-inch focus lens, and so on. The collimating and telescope lenses are of quartz of opposite rotations.

A focussing screen of ground glass is always provided in order to get the apparatus into preliminary adjustment, but often the lines in the spectrum used will seem absolutely distinct on the ground glass, and will not appear quite so good when a photograph is taken. The final adjustment has then to be made by racking the back a tiny amount nearer to the lens, say a twentieth of a turn of the pinion, and

taking one photograph, then racking the back slightly further away from the lens—a *tenth* of a turn of the pinion—and taking another photograph. On developing the plates, and examining the lines in each negative with a magnifying-

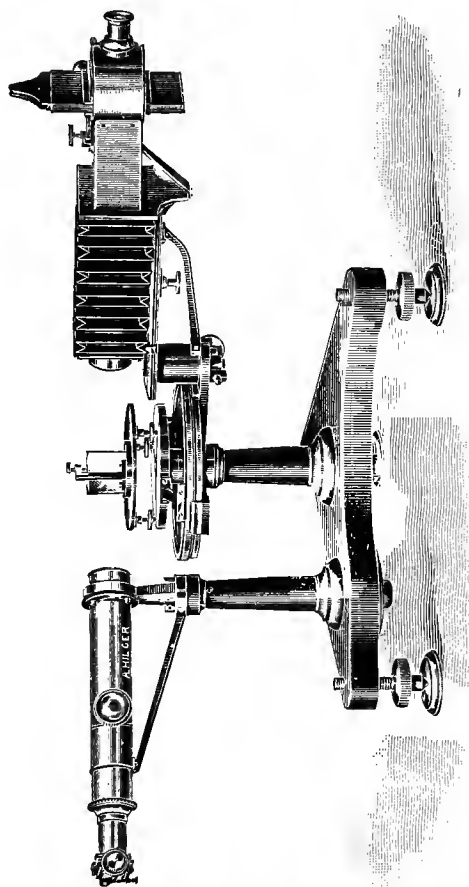


FIG. 46.

glass, we shall see which position gives the better definition—*i.e.*, a twentieth of a turn nearer to, or further away from, the lens than the position found by *focussing*. More trials may be necessary before the best results are obtained.

Accurate wave-length determinations are usually carried out by examining a spectrogram of the unknown spectrum taken against, or overlapping, a known spectrum by means of a *travelling microscope*. The known spectrum may be the combined arc spectrum of Ca, Li, Na, Tl, etc., or if more lines be desired, the iron arc spectrum, or the air-spark spectrum, etc. The wave-length of the unknown lines are obtained by interpolation. The travelling microscope consists of a microscope which can be racked along a horizontal stage, on which latter the negative is fixed; the amount of movement—*i.e.*, the distance through which the microscope is racked in order to move it from one line to another—is read off by means of an accurately divided micrometer screw. The eye-piece is provided with cross-wires, and if a known line coincide with first these and then an unknown line, the micrometer screw will give the necessary reading to determine the distance between the two lines.

If  $L$  be the distance between two *closely adjacent* known lines, and  $l$  be the distance between one of the known lines and an unknown line to be determined, and  $\lambda_1$ ,  $\lambda_2$  be the wave-lengths of the known, and  $\lambda_3$  that of the unknown lines, then

$$\frac{\lambda_3 - \lambda_1}{\lambda_2 - \lambda_1} = \frac{l}{L}.$$

Or *Hartmann's interpolation formula* could be used :

$$\lambda_3 = \lambda_1 + \frac{c}{\theta_3 - \theta_1},$$

where  $\lambda_3$  is the wave-length of the unknown line,  $\lambda_1$  that of a known line, and  $\theta_3$ ,  $\theta_1$  their respective angular deviations,  $c$  being a constant which has to be determined.

We shall next describe the construction of a *simple spectrograph* suitable for ordinary inorganic chemical analysis or absorption band determination, made with a grating replica,

as this enables quite a long spectrum to be obtained with a camera of very modest dimensions.

The design of the spectrograph is shown in Fig. 48, in as simple a form as possible. In Fig. 47, a neat rectangular wooden box, takes the place of the collimating telescope, and S is the slit attached to the front, and  $L_1$  an achromatic meniscus lens, the distance SL being the focal length of  $L_1$ , so that all rays emerge from  $L_1$  parallel. Placed normally to the

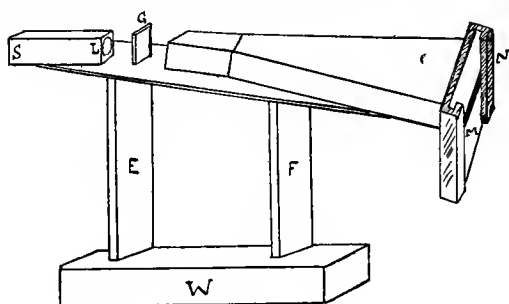


FIG. 47.

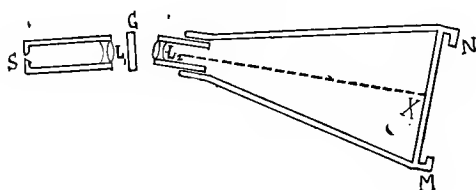


FIG. 48.

axis of  $L_1$  is a plain grating or replica G, and the diffracted beam is received by the telescope lens  $L_2$ , which is fitted to the front of another, shorter, rectangular box, which can slide inwards or outwards within a slightly larger rectangular box, which opens outwards at PQ, so that at MN the whole spectrum is included. If X is the centre of MN, and  $L_2$  the centre of the lens, the line  $L_2X$  must make an angle with the axis of the collimator  $=\theta$ , where  $b \sin \theta$  is the wave-length of the central ray of light in the spectrum MN. The grating

G must be fixed at the point where the line  $XL_2$  produced meets the axis of the collimator. The spectrograph is seen in elevation in Fig. 46, B, where the base-board, to which the collimator, grating, and camera are attached, is fixed by two stout wooden uprights, E and F, to a heavy wooden block, W. The camera back is arranged with grooves to take either a focussing screen or a dark-slide; the spectrum appears on the plate at MN, a long rectangular opening in the back permitting it to act on the plate. By shifting the dark-slide further down the grooved back between each exposure several photographs may be taken on the one plate.

Such a spectrograph can be made at a very small cost with the help of a carpenter, and for the convenience of the reader the following dimensions are given of one in actual use by the author, which gives a 5-inch spectrum between  $\lambda = 3500$  and  $\lambda = 7500$ :

Focal length of collimating lens	10 cm.
Diameter       "       "	3'2 cm.
Dimensions of collimating 'box'	10 × 10 × 6 cm.
Grating (replica made by Mr. Wallace, of Yerkes Observatory, Chicago)-	15,150 lines per inch.
Observatory, Chicago)-	
Objective lens, focal length - -	45 cm.
Diameter of same	3'2 cm.
Dimensions of base of camera body	46 × 46 × 6 × 15 cm.
"       side of same	46 × 6 cm.
Camera back (takes a 5 × 4 inch dark-slide)	15 × 15 cm.
Size of opening in the back—i.e., size of spectrum -	12'5 × 1 cm.

The size of a 5 × 4 inch plate being approximately 12'5 × 10 cm., at least six photographs can be taken on one plate, allowing a space of about 5 cm. between each.



The camera portion may also be made movable about a centre at G, so that different portions of the spectrum, or a first or second order spectrum, can be photographed at will.

It may be remarked that the distance between objective and plate should be practically equal to the focal length of the lens.

A simpler form of spectrographic camera may be made as indicated in Fig. 49. A narrow rectangular box, ABCDE, is made, with a slit at S, and two achromatic meniscus lenses,  $L_1$  and  $L_2$ , arranged with a grating replica, G, between them, the axis of  $L_2$  being normal to the plate, which receives the spec-

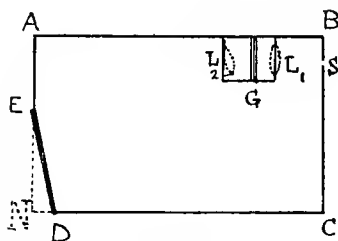


FIG. 49.

trum at ED, the portion EDN being cut away, and some simple form of a grooved arrangement placed at ED to take a dark-slide. By using lenses of short focal length a long spectrum is obtained at ED, the distance between the slit and  $L_1$  being much less than its focal length.

The lenses  $L_2$  and  $L_1$  with the grating between are fixed in a wooden block, which can be slid nearer to or further away from the slit for focussing purposes.

In this form of camera, where the rays from the slit do not emerge parallel from the lens  $L_1$ , the whole of the emergent light is not utilized, as it cannot all be embraced by the lens  $L_2$ . Great care must be taken when focussing and adjusting the arrangements to have the light source and any lens used to illuminate the slit in a line with the slit, and

in all work done with the camera these conditions must again be fulfilled.

Such a camera can be made to readily separate the yellow sodium lines, and these should be seen separated on the focussing screen, when examined with a small magnifying-glass, when making the final adjustments.

The arc flame is a very convenient source of light with which to adjust such a spectrograph, the poles being brushed over with some lithium chloride solution; the blue, orange, and red lithium lines will then be seen, also the D lines, and the violet lines due to the calcium present in the carbons. If all these lines be brought into distinct focus, the whole spectrum may be regarded as satisfactorily defined.

One precaution must be taken in all spectrographic work—viz., to avoid any scattered or other light reaching the plate. The inside of every tube or wooden compartment must be dead-black, and in the case of a spectroscope with photo attachment or such an arrangement as shown in Fig. 47 the grating or prism must be covered over with black cloth or velvet, and every likely inlet of light carefully stopped up.

A good test for *scattered white light* may be carried out by exposing a plate in the camera for two or three minutes without illuminating the slit with any light source; if on development no silver deposit (*i.e.*, image) appears on the plate in the position which the spectrum would occupy, it may be taken for granted that the camera is quite light tight, and proof against scattered light.

The *resolution* obtainable with a *spectrograph* depends upon the width of the slit, the resolving power of the dispersing apparatus, and the length of the spectrum as received by the photographic plate. Certain qualities are necessary in the plate itself in order that the full benefit of resolution may be obtained. Thus, if the spectrograph clearly resolve two

lines of wave-length  $\lambda_1$  and  $\lambda_2$ , so that they are separated by a distance  $d$ , but the grain of the plate be so coarse that in the negative image the particles of reduced silver are of a diameter  $>d$ , then the separation of the lines will be indistinct, and possibly not observable.

Suppose the spectrograph photographs the spectrum between  $\lambda = 3000$  and  $\lambda = 7000$  A.U., and that this occupies a length of  $L$  cm. on the plate; also that it is wished that two lines whose wave-lengths differ by  $n$  units be clearly separated in the photograph. Then the distance in cm. between two such lines will be

$$\frac{n}{4000} \times L.$$

Now, assuming that the lines are infinitely narrow, the *size of the grains* must be less than half this amount, as if grains appeared with their centres on the centre of each line, and

were equal in diameter to  $\frac{n}{4000} \times L$ , they would meet, and

the two lines would therefore run into one another and not be resolved. Hence, if the least size of grain permissible, or the *resolving coefficient*\* of the plate, be denoted by  $\tau$ , then the condition for the desired resolution becomes

$$\tau < \frac{n}{4000} \times L.$$

The grains of reduced silver in a negative which has been normally developed can be determined by means of a photomicrograph, a micrometer eye-piece being used. Although under a high power these 'grains' may often be seen to be clumps of still smaller grains, it is the clumps that determine the conditions for distinct resolution.

The choice of sensitive plates for use in spectrographic

\* *Photographic Journal*, April, 1906.

work will be discussed in the next chapter, and we have now to consider the method of *scaling a spectrograph* so that rough wave-length determinations can be made. The method is similar to that described for the prism spectroscope, but we have to deal with positions on the plate instead of angular deviations.

A photograph is first taken of a line spectrum, such as that given by a hydrogen or mercury vacuum tube; better still it is to use a line spectrum as given by the arc, as in order to make an accurate scale the more lines chosen the better. In the little cameras made with grating replicas, such as already described, it will suffice to have a few lines only, as the curve is almost a straight line, being bowed simply because every point in the plate is at a slightly different distance from the objective lens.

A piece of squared paper is taken, and two axes drawn at right angles; wave-lengths are plotted along one axis, and along the other are plotted the positions occupied by the lines of known wave-length. Oscillation frequencies may, of course, be used instead of wave-lengths if preferred. Several points may be obtained which, when joined together by a freehand curve, give the necessary curve for the spectrograph.

To take an actual example, suppose the length of the spectrum photographed be 15 cm., and that this includes the region between 3,000 A.U. and 7,500 A.U. There is, therefore, a region corresponding to 300 units represented by each centimetre, neglecting the abnormality above referred to. Suppose the axes be drawn about 60 cm. in length; the axis corresponding to positions of lines in the negative is therefore about four times the actual length of the negative. Taking the two lines H and D in a negative, mark H (3,969 A.U.) along the axis O A, about 14 cm. from O. Now carefully ascertain with a good pair of dividers the distance between

H and D (5,893 A.U.) in the negative; and at four times this distance mark D on the axis O A. Similarly, mark as many known lines as possible on O A, so that O A eventually corresponds to the negative, except that it is four times its length. Points are then marked on the squared paper where the abscissæ and their corresponding wave-length ordinates meet, and these points, when connected up, give the curve of the spectrograph.

Two little *spectrographic cameras* which deserve notice are those sold by Messrs. Sanger-Shepherd\* and Messrs. Penrose† respectively. The former gives a 3-inch spectrum, including the violet to the red at about 7,000 A.U., and is dependent on a small direct-vision prismatic spectroscope for the dispersion. The latter gives a spectrum of similar length, but a prism-grating (replica) is used for the dispersion, so that the distribution of colour is fairly, though not altogether, normal. The camera back is arranged in each so as to take a quarter-plate dark slide, which enables, by lateral shifting, four or five spectra to be taken on one plate  $4\frac{1}{4}$  by  $3\frac{1}{4}$  inches. By adjusting the slit, fairly fine resolution can be obtained, but the cameras are really designed for the testing of colour sensitiveness in plates (see Chapter VII.), or for testing absorptions of dyes or other coloured substances.

The natural-colour photograph of the spectrum given in the frontispiece was taken with the Tallent spectrographic camera (Penrose), and the other photographs were taken with the Sanger-Shepherd instrument. Many larger spectrographs, of somewhat similar design, and capable of far more critical work, are made by the latter firm, and too much cannot be said of their fine workmanship.

In Fig. 50 will be seen the scale of a 3-inch Sanger-Shepherd spectrograph.

\* Gray's Inn Passage, Red Lion Street, London, W.C.

† Farringdon Road, London, E.C.

SIMPLE METHODS OF CHEMICAL SPECTROGRAPHIC ANALYSIS  
(INORGANIC).

1. *Comparison with a known Line Spectrum*—(a) *Electric Arc*.—Some known lines are necessary in the spectrum, and these may be obtained by first making an exposure with the flame of the arc focussed on the slit of the spectrograph, the poles having been moistened with a solution of lithium chloride. This will give the lines at 4,602, 6,104, and 6,708, whilst the D lines, the H and K, and the green nitrogen and *b* lines, are also sure to make their appearance. The dark slide is then slightly shifted, so that a portion of the unknown spectrum is photographed on the top of the known spectrum. To obtain the unknown spectrum, either a fresh, purified negative carbon rod may be substituted for the one already used, or an ordinary rod which has been soaked in a concentrated solution of the substance under examination; or even some of this solution may be brushed over the negative rod already used.

It is customary in some laboratories to obtain the known lines and the unknown in the one exposure by using carbons which have been soaked in a solution of a known salt, and brushing the pole with the unknown solution, or boring a vertical central hole in the top of the rod and packing it with some of the substance under examination. The advantage of having the known and unknown spectra partially overlapping is that, should the latter contain some of the known metal, it will be more readily discovered.

(b) *Flame Spectra*.—Very long exposures are required with flame spectra, and visual examination is to be preferred.

The developed negative should be allowed to dry before it is examined. By means of dividers, the distance between the known and the principal unknown lines is measured, and thence, by reference to the spectrograph scale, the wavelengths of the latter are ascertained.

Or, a large cardboard scale, with a scale of wave-lengths marked on it, which has been accurately drawn from negatives of several known lines, is hung on the walls, and an optical lantern placed before it; the spectro-photograph to be examined is placed in the lantern, and its image cast upon the cardboard scale, just like a lantern-slide is thrown upon a screen. The position of the lantern is so adjusted that

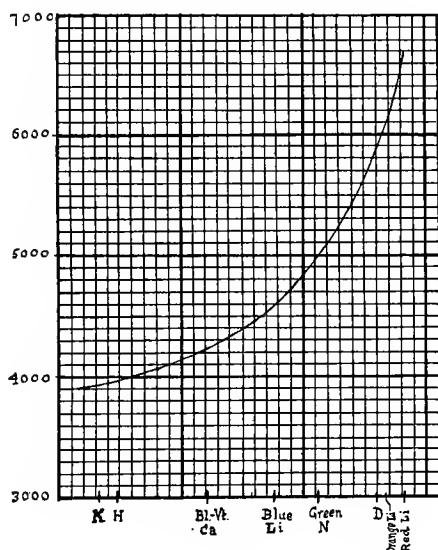


Fig. 50.

the known lines in the spectrum coincide with their correct wave-lengths on the cardboard scale; the wave-lengths of all lines in the negative may then be instantly read off on the scale. This method is particularly useful where the spectrograph is small—quarter-plate, for instance—if larger, a special-sized optical lantern will of course be necessary.

2. *Comparison with a known Line Spectrum (Electric Spark).*—The procedure may be much the same as before,

suitable means of introducing the substance under examination into the spark being employed.

Great care must be taken to avoid any shifting of the lines between the exposures on a known and an unknown substance. In other words, the spark, the condensing lens, and the slit, must be in a line, and neither of the two former must be shifted, otherwise the spectra may be slightly displaced one towards the other. If the spark be surrounded by air, as it is under ordinary circumstances, the air-lines should suffice to locate the unknown lines. If the air-lines are not wanted, the two points between which the discharge takes place should be brought very close together, and the Leyden jar or set of jars regulated to get the most metallic lines, or the discharge from the point where the brightest metallic lines are seen, near to that point, may be focussed on the slit; self-induction may also be utilized, if necessary, to reduce the air-lines.

The *development of spectrographic 'negatives'* will be discussed in the next chapter, in connexion with the testing of colour-sensitive plates. But it may be here observed that any ordinary developer will answer the purpose, the chief requirements being—(1) clean-working qualities; (2) contrast-giving power; (3) quickness in action. A concentrated metol-hydroquinone developer, such as that given at p. 95, is therefore very suitable. The exposure of a plate in the spectrograph should, if possible, be such that the bright lines are not excessively overexposed, and therefore over-dense and *widened* by the spreading action of the light in the sensitive film; the finer the lines, the easier it will be to accurately find their wave-lengths. It is sometimes a convenience to make two exposures, one shorter than the other, the dark-slide being shifted between each so that the two photographs just touch. The principal lines only will then appear in the least exposed photographs, and they will



be very fine, and will thus show the centres of the thicker and overexposed principal lines in the most exposed photograph, in which the weakest lines will, of course, appear also.

It is often convenient to *intensify* a negative which has been underexposed in the spectrograph. Spark and vacuum-tube exposures are often very long, and even then the lines in the photograph are very feeble. They may be greatly intensified with less trouble, sometimes, than would be entailed in making another exposure.

The best procedure is as follows: The negative is very thoroughly washed after fixing, and is then placed in a solution of

Mercuric chloride	6.4 gm.
Ammonium chloride	2.7 gm.
Water	250 c.c.

It is left in this until the image appears quite white, or 'bleached.' It is then washed in running water for ten minutes, and next placed for five minutes in a 10 per cent. solution of ammonia (specific gravity 0.880), where it re-blackens and gains intensity. The procedure may be repeated if after a first treatment further intensification seems desirable.

*Halation* is a technical fault which often crops up in spectrographic work, rendering lines which should be quite distinct more or less blurred, owing to a light ray, such as AB (Fig. 51), passing through the film into the glass and suffering reflection from the back of the glass at P, thus again acting on the film at Q, in a different position. Halation can be avoided by applying what is known as a *backing* medium to the back of the plate, this being a perfectly absorbent medium of the same refractive index as that of the glass itself. Light which passes through the

glass then enters the backing, which is, of course, in optical contact with the glass, and is absorbed. To be opaque to all rays it is essential that the backing be black, and this should be borne in mind when ordering commercial backed plates. A backing medium can be made by adding sufficient Indian ink or some soluble dead black substance to a paste of yellow dextrin and water; a little spirit may be added to

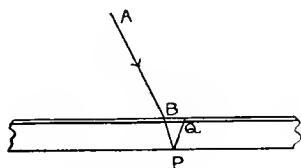


FIG. 51.

accelerate the drying. The backing is applied with a piece of sponge to the glass, the work being done in the dark-room, and the backed plates are then placed in a rack and kept in darkness until the medium is dry. It is removed before developments with the aid of a finger-tip, by holding the plate under the tap; the film side should then be washed, in case any backing has found its way on to the surface.

## CHAPTER VII

The colour sensitiveness of plates for spectrography—Commercial plates—Bathing plates—Special methods of red-sensitizing—Testing plates for colour sensitiveness—Measuring densities in spectrum negatives photometrically—Interpretation of results—Theory of colour-sensitizing.

AN ordinary photographic dry plate is only sensitive to rays of light of wave-lengths between about 2,200 A.U., and 5,200 A.U. With prolonged exposure an ordinary plate can be made to record green-yellow and red rays, but it is quite unsuitable for spectrographic work. Owing to the limit in *colour sensitiveness of gelatino-bromide plates* (and gelatino-bromo-iodide plates) a great deal of the spectrographic work that has been done—and is still being done—has been confined to the ultra-violet and blue-violet regions of the spectrum, and much scope for investigation yet remains in red and infra-red spectrography.

It was found by *Waterhouse, Vogel*, and others, nearly thirty years ago, that by adding certain dyes to the emulsion with which plates are coated the plates became sensitive to coloured rays which hardly affected them in the ordinary way. Thus eosin and erythrosin were found to render the plates sensitive to the yellow-green rays, so that they possessed this sensitiveness in addition to their normal blue-violet and ultra-violet sensitiveness. The work of *colour-sensitizing* has been slowly followed up until the present time, and just recently the subject has received a vast

amount of attention, more particularly owing to the discovery of the very high powers of colour-sensitizing which are possessed by certain of the cyanin and *iso-cyanin* derivatives.

If the work anticipated is to be done in the region between 2,000 A.U. and 5,000 A.U., ordinary photographic plates will answer the purpose perfectly. If the whole visible spectrum is required, a good colour-sensitive or 'panchromatic' plate must be selected. There are a few reliable makes on the market at the present time, but it will be found very advantageous, where possible, to employ bathed plates—*i.e.*, ordinary plates colour-sensitized a day or two before use by means of a solution of some suitable panchromatizing dye.

Many commercial colour-sensitive plates are prepared to resist the action of the ultra-violet rays, as these, being invisible, should not be allowed to take part in the production of an ordinary photograph. They should therefore be avoided where the ultra-violet region is under examination.

What is required for spectrography is a plate which is fairly evenly sensitive to the whole spectrum, which is of as great rapidity as possible, possesses a very fine grain, and works—*i.e.*, develops—with great cleanness. The Mawson B orthochromatic plate, the Gem Tricol, the Wratten panchromatic, the Sanger-Shepherd 'Colour' plate, and the Imperial special sensitive orthochrome, are five varieties which can be recommended from actual experience, each possessing a fair amount of green sensitiveness (so difficult to obtain), and sufficient red sensitiveness to record lines of wave-length 6,500 or 6,700 A.U.

The size of grain is to some extent dependent on the developer used and the length of development, and therefore, if a plate is to be examined to see whether it be suitable for a certain degree of resolution, it should be developed under conditions to which it is likely to be subject in actual work.

In the writer's own work, four minutes' development at  $13^{\circ}$  C. is given to the plates with a special developer under ordinary circumstances. It will be found very desirable to fix some such standard conditions for working, as otherwise no uniformity in the results can be obtained.

The special developer referred to is a very concentrated and energetic one, and is prepared as follows :

Distilled water	- 1,000 c.c.
Metol -	12.5 gm.
Sodium sulphite (cryst.)	67.5 "
Sodium carbonate (cryst.)	67.5 "

One drop to each 30 c.c. of a 10 per cent. solution of potassium bromide is added, or 0.25 gm. of the bromide may be conveniently mixed with the above quantity of developer. The ingredients should be added in the order given.

Another developer, which is rather less vigorous, but gives greater density and contrast, deserves mention, and is as follows :

Distilled water	1,200 c.c.
Metol -	1.25 gm.
Potassium metabisulphite	1.25 gm.
Hydroquinone	4 "
Sodium sulphite (cryst.)	30 "
Sodium carbonate (cryst.)	52.5 "
Potassium bromide -	0.4 "

At a temperature of  $13^{\circ}$  C. eight minutes may be given with this developer.

Owing to the red sensitiveness of the plates, as little ruby light as possible should be used in the dark-room, and during development the dish should be covered over with an old cardboard-box lid or other suitable cover.

After development the plate should be slightly rinsed, and then placed for ten minutes in an acid fixing-bath prepared thus :

Water	-	1,000 c.c.
Sodium thiosulphate		400 gm.
Sodium bisulphite		20 „

All negatives should be thoroughly washed, *and dried*, before being examined critically.

Commercial panchromatic plates have many advantages, and are exceedingly convenient, but very often it will be found desirable to colour-sensitize one's own plates, especially since an ordinary plate of very fine grain can be chosen, such as a photo-mechanical or slow 'Ordinary' plate.

A very weak solution of a suitable dye is prepared, and in a perfectly clean porcelain dish one or more plates (according to the size of the dish) are laid, film upwards, and over them is poured the solution. Needless to say, this is done in ruby light, or in a 'safe light.'\* The dish is gently rocked for three minutes, and the dye solution is then poured off, and the dish placed under a running tap for a further three minutes, during which time the excess of dye is washed out of the films. Ten changes of a minute each in distilled water is preferred by some for this washing. The washed plates are stood in a clean grooved wooden drying-rack, and allowed to dry in a perfectly dark room, which should be dust-proof, and, if possible, warm ; it must also be free from chemical fumes. The more rapid the drying, the better will be the results. Finally, 'bathed plates' should be used, if possible, within a day or two of being prepared, as they will not usually keep very well.

\* Many dyes induce great red sensitiveness, but little green sensitiveness, when a pure, dull green light will be safer than red.

The following solutions will be found suitable for bathing plates :

*For the Region between D and b.*

Water	-	90 c.c.
1 per cent. alcohol solution of	}	2 c.c.
<i>erythrosin</i>		
10 per cent. ammonia solution		10 c.c.

*For the Region between E and D $\frac{1}{2}$  C.*

Water		90 cm.
1 per cent. alcohol solution of	}	2 c.c.
<i>rhodamin B</i>		
10 per cent. ammonia solution	-	10 c.c.

*For Complete Colour Sensitiveness to about  $\lambda = 6700$  A.U.*

Water	-	90 c.c.
1 per cent. alcohol solution of	}	1 c.c.
<i>pinachrom</i> or <i>homocol</i>		
10 per cent. ammonia solution		10 c.c.

*For Red Sensitiveness between  $\lambda = 5800$  and  $\lambda = 7200$  A.U.*

Water	-	99 c.c.
0.05 per cent. alcohol solution of	}	1 c.c.
<i>pinacyanol</i>		

*An Alternative Bath.*

Water	-	75 c.c.
0.1 per cent. aqueous solution of	}	3 c.c.
<i>diazo black BHN</i>		
10 per cent. ammonia solution		20 c.c.
Special silver solution*	-	2 c.c.

\* For the composition of this solution, see p. 100.

Other dyes which may be successfully used for bathing are *pericol*,<sup>†</sup> *isocol*,<sup>†</sup> *pinaverdol*, *dicyanin*, *ethyl cyanin*, *orthochrom T*. These may be obtained of Fuerst Brothers, of Philpot Lane, E.C., except those marked (†), which are supplied by the Bayer Co., of 19, St. Dunstan's Lane, E.C.

It is a very difficult matter to obtain plates which are sensitive to the rays of wave-length greater than 7000 A.U., but two methods deserve mention—one a purely physical method, the other a dye method.

Silver bromide, as will be explained later on, may be obtained in various physical states, its potential energy varying with the method in which it is prepared. Thus it is well known that an emulsion of silver bromide becomes more sensitive to light when it has been cooked at a high temperature for some time. But in all states it is apparently sensitive to the whole spectrum—at any rate, between 1000 and 20,000 A.U.—its sensitiveness varying very greatly according to the wave-length of the light. By preparing the silver bromide in a special way it can be made far more sensitive to the red and infra-red rays than otherwise, and the method adopted by *Ritz* and others has been to precipitate it by mixing solutions of a soluble bromide, such as KBr and silver nitrate, washing the precipitated haloid, and heating it for some time. It is then emulsified with gelatin, and the emulsion coated upon glass. *Abney's* method was to prepare a *collodion emulsion* of silver bromide of a bluish colour by transmitted light, so that it absorbed the red rays. This was done by a somewhat complicated procedure, which very few experimenters have been able to repeat with any success. Abney, however, mapped the solar spectrum by means of spectrographs taken with this emulsion, as far as 20,000 A.U.

The easiest and most promising method of photographing the red and infra-red region between about  $\lambda = 6000$  and



$\lambda=9000$  A.U. has been found by the writer to depend on the use of a washed collodion emulsion (such as Dr. Albert's, supplied by Messrs. Penrose and Co.), and the employment of *benzo green BB* (Bayer) for colour-sensitizing.

A perfectly clean piece of glass of the requisite size for the spectrograph is well polished with a piece of soft, pure tissue-paper, and is then painted round the edges (of the side to be coated with emulsion) with a rubber edging solution, made by dissolving pure rubber in benzol. The glass is

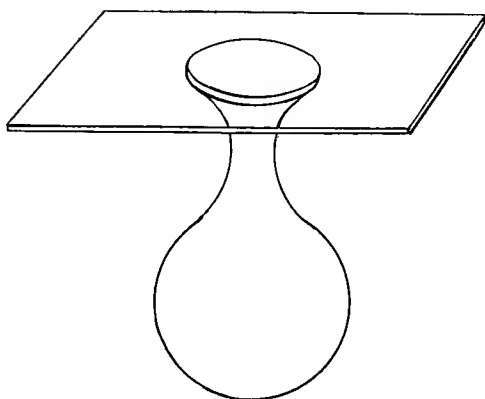


FIG. 52.

now held by means of a pneumatic holder (Fig. 53), the 'edged' side upwards, and in the dark-room sufficient of the washed collodion emulsion is poured in a pool on the centre of the plate to easily cover it when it is tilted in all directions. The surplus emulsion is drained off, and the plate meantime given a side-to-side motion to ensure even setting of the emulsion. After one minute enough of the following solution is poured on the plate to well cover it, the collodio-bromide film allowed to remain thereon for one minute, and then poured off:

Benzo green 1 per cent. aqueous solution	1 c.c.
Distilled water -	5 „
Alcohol -	25 „
Special silver solution (see below)	1 „
Concentrated ammonia	1 „

This solution keeps good for several weeks if kept below 15° C.

The plate is exposed whilst wet in the spectrograph, and is afterwards washed under a running tap for one minute, and is then developed for two to three minutes in a metol-hydroquinone or glycin developer. Care must be taken to avoid touching the film with the fingers, as it easily rubs away. It is fixed for two minutes in an ordinary bath, and finally washed for ten minutes. When dry it may with advantage be varnished to protect the very sensitive film.

The special silver solution, already twice referred to, is made up as follows:

Silver nitrate	2 gm.
Concentrated ammonia	2 c.c.
Distilled water -	to 100 „

Owing to the high red sensitiveness of the plates, a good deal of fog will be experienced if the temperature of the room be high. The experimental work had, when working out this method, to be postponed during the summer months, and the greatest success was obtained when the laboratory could be kept at 5° C., or slightly under. Negatives of absolute cleanliness were then obtained without any difficulty. The *infra-red solar spectrum* between  $\lambda = 7500$  and  $\lambda = 9500$  A.U. has been photographed recently\* by Millochau, the plates being sensitized by immersing them for about ten minutes in distilled water acidulated with acetic acid, then

\* *Comptes Rendus*, 1907, xiv., 725.

in a saturated alcoholic solution of *malachite green*, and finally washing and drying them. They were rendered much more sensitive by exposing them for thirty seconds at a distance of 75 cm. to a 4 candle-power electric light, according to the method suggested by *Waterhouse* in 1875.

The preparation of plates sensitive to the extreme ultra-violet must next be briefly touched upon. *Gelatin* varies in its powers of absorbing the ultra-violet rays, but begins to take effect at  $\lambda = 2000$  A.U. A plate containing no gelatin or other vehicle is therefore desirable, and such a one has been prepared by *Schumann* and others, by precipitating pure silver bromide upon an absolutely clean piece of glass.

The following is the outline of the simplest method: Two grams of potassium bromide are dissolved in 4 litres of dissolved water, and 2 grams of silver nitrate are dissolved in 100 c.c. of distilled water; in the dark-room the silver solution is added a little at a time to the bromide solution, vigorous shaking being given after each addition. The transparent reddish-coloured solution thus produced is filtered and then placed in an absolutely clean vessel, at the bottom of which is a perfectly clean piece of glass; it is left untouched for two days, during which time a fine deposit of pure silver bromide will settle on the plate. When removing the plate after this period, care must be taken to keep it horizontal, and not to touch the 'film' with the fingers. A pyrogallol developer is recommended for the development of such plates, which are extremely slow, and therefore require a considerable exposure.

Further methods of preparing these plates, in which a small quantity of gelatin is used to render the emulsification, setting, etc., better, will be found on reference to the *Wiener Berichte*, 102, II.A, 994 (1893).

According to *Eder*, silver chloride (subsequently developed, not printed out) possesses sensitiveness extending to N, and

having its maximum at about the line H, whilst the maximum sensitiveness of silver bromide emulsion is to the red side of the G line. For work in the extreme violet, chloride plates are therefore useful, but they are considerably slower than the ordinary bromide or bromo-iodide plates.

The testing of plates for colour sensitiveness is an extremely interesting branch of spectrographic work, and becomes necessary if we wish to choose a plate best suited for certain purposes, or if light filters have to be prepared

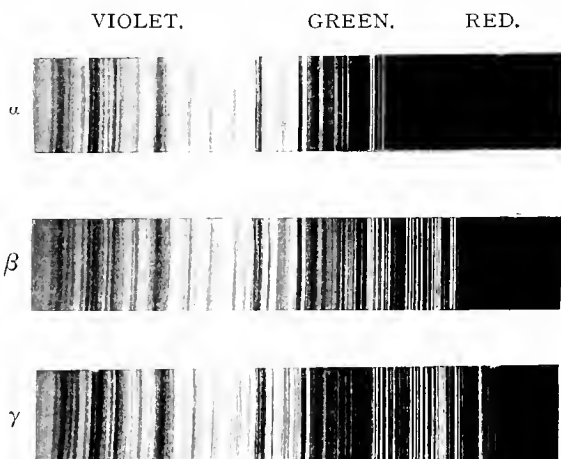


FIG. 53.

for photo-micrography, orthochromatic or three-colour photography. It is, of course, most essential when the colour-sensitizing action of dyes is to be investigated, as we have then to test for colour sensitiveness plates which have been bathed with the dye against unbathed plates, and to find the precise action of the dye by the difference in the two results.

One method of finding to what extent the sensitiveness goes is to photograph a line spectrum on the plates, and find the wave-lengths of the last lines recorded on each. Thus in

Fig. 53 will be seen the spectrum of the iron arc, photographed, in the case of  $\alpha$ , on an ordinary slow bromo-iodide plate; of  $\beta$ , on a commercial green-yellow sensitive plate; and of  $\gamma$ , on a commercial panchromatic plate. The colour sensitiveness of  $\alpha$  extends to at least  $\lambda=5500$  A.U., of  $\beta$  to at least  $\lambda=5893$  A.U., and of  $\gamma$  to at least  $\gamma=6400$  A.U. The term 'at least' is used, since on prolonged exposure it is always possible to record light of larger wave-length than is recorded on a normal or shorter exposure.

Whilst the use of a line spectrum serves to show the extreme limits of sensitiveness of a plate, a continuous spectrum is necessary in order to *test a plate for its distribution of colour sensitiveness*, and this is what one more particularly wishes to ascertain when testing either commercial plates or experimental bathed ones.

Some recognized source of white light must be employed, such as the positive pole of the arc, incandescent gas-light, or *lime-light*, etc. The latter will be found very convenient, particularly as one pure lime cylinder can be removed from the jet and another lime inserted in its place which has been brushed with a solution of, perhaps, lithium and thallium chlorides. If a second exposure be given by means of the heated lime, partly overlapping the other exposure, some datum lines are obtained which are very useful for referring the result to the scale of the spectrograph. It is worth noting that, to get lines from a lime-light source most powerfully, a slight excess of coal-gas or an insufficient supply of oxygen is necessary, assuming an oxygen-coal-gas jet be used.

Daylight can be used as the source of light if the reader possess a heliostat, and the Fraunhofer lines are then very useful for locating the various regions of the spectrum.

It is desirable, if possible, to have the same source of light always, and to have it in the same position relative to the slit, a condensing lens being used also, and this, too, being in

a fixed position. Some reasonable period of exposure must then be fixed upon, and similarly some fixed time of development at a constant temperature. It is interesting, also, to make several exposures on the one plate, of times  $T$ ,  $nT$ ,  $n^2T$ ,  $n^3T$ , etc., or else  $T$ ,  $nT$ ,  $2nT$ ,  $3nT$ , etc.

*Development* should not be carried too far, as, if possible, the densities of the negatives should be obtained by means of a *photometer*. For this reason the plain metol developer given on p. 95 is strongly recommended, as it does not too readily yield density, whilst it gives the full record of the exposure.

The dry negative of the spectrum is marked off into equal regions by referring it to the scale, and the density of each region ascertained by means of a photometer. In a given instance the following result was obtained:

Region (in A.U.).	Densities of the Negative.
3900-4100	0·10
4100-4300	1·42
4300-4500	2·05
4500-4700	2·27
4700-4900	1·98
4900-5100	1·72
5100-5300	1·96
5300-5500	2·47
5500-5700	2·29
5700-5900	0·81
5900-6100	0·11

These densities, plotted against wave-lengths, provide a curve (Fig. 54) showing the colour-sensitiveness of the plate in question.

In order to accurately determine the effect of a given dye, the writer prefers to take two plates and bathe one of them

only; to then cut off a strip of the unbathed and bathed plates, and ascertain their relative speeds by some system such as that of *Hürter and Driffed*.<sup>\*</sup> The two plates are then exposed in the spectrograph for times inversely as their speed. Thus, if the unbathed plate were of speed  $s$ , and the bathed  $s_1$ , they would be respectively exposed for times  $s_1T$  and  $sT$ ; the speed determination and the spectrograph exposures both being made with the same source of illumination.

Most dyes affect the rate of development of the plates

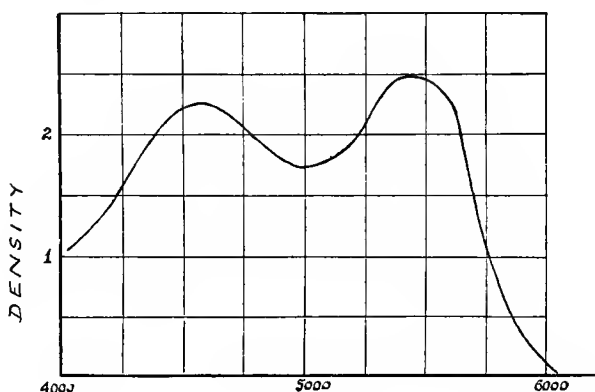


FIG. 54.

bathed, and a determination of the relative speeds of development should, therefore, if possible, be made,<sup>\*</sup> and times varying inversely as the development factor given to the unbathed and bathed plates. The densities of the two negatives corresponding to equal regions of the spectrum are then obtained, and those for the *unbathed* plate subtracted from those obtained for the *bathed* plate; the differences between the two give the actual effect of the dye in question, and if plotted against wave-lengths, will provide a curve of

<sup>\*</sup> *Vide* 'The Photo Miniature': the H. and D. System.

the enhancement of colour sensitiveness. Such a curve is given in Fig. 55 for the sodium salt of fluorescein tetriodide (*erythrosin*).

The densities ascertained in each portion of the spectrum negative read are logarithms of the *opacity* of the film. A convenient photometer for reading densities in spectrum

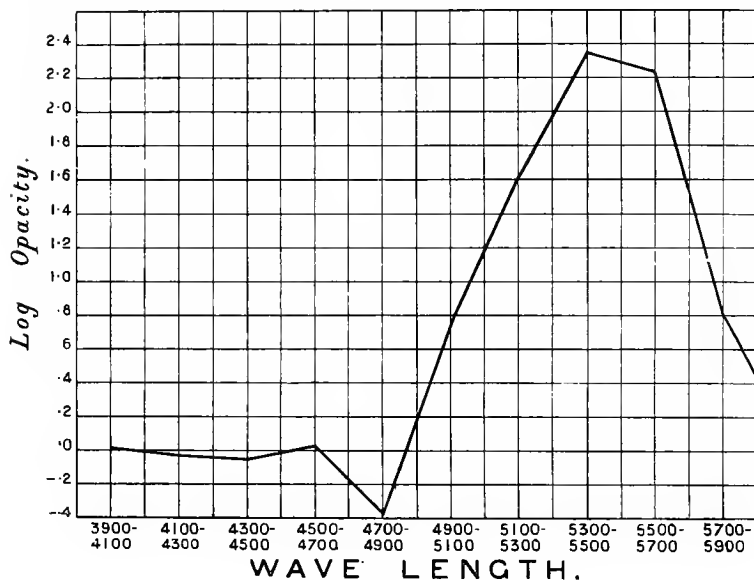


FIG. 55.

negatives is shown in diagram form in Fig. 56, and represents a reading photometer designed for sensitometric photographic work. Two equal sources of light,  $L_1$ ,  $L_2$ , are fixed at each end of a dark box, inside which is a grease-spot or Lummer-Brodhun photometer  $P$ , and this moves by rack and pinion up and down a scaled slide  $S_1$ ,  $S_2$ . The photometer is lighted from each side by means of apertures  $A_1$ ,  $A_2$ , and when in the central position at  $O$  the two sides of the greased parchment appear equally bright, and are both



seen at once by means of two mirrors placed as shown in Fig. 56, *a*.  $S_1, S_2$  is a logarithmic scale, and if the negative be slid along through the grooved arrangement at H, P has to be brought nearer to  $A_1$ , according to the density of that portion of the negative immediately in front of the aperture  $A_1$ . Thus, if for two successive portions of the negative the positions of P had to be  $d$  and  $f$ , in order that both sides of the greased parchment looked equally bright in each respective case, and  $A_1 d = 2 A_1 f$ , then the negative would be doubly as dense in the portion when P was at  $d$  as in the

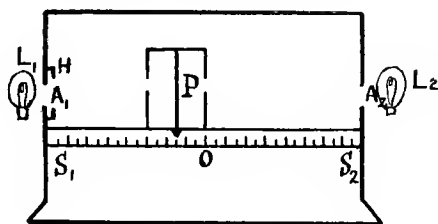


FIG. 56.

*a*

portion when P was at  $f$ . A certain amount of light scatter, which takes place within the film, causes some risk of inaccuracy.

In conclusion of this chapter, we shall deal with the *theory of the sensitizing action of anilin dyes* on the photographic film. It must first of all be pointed out that, since silver bromide *per se* is sensitive to a greater or less extent to light of practically all wave-lengths, the action of the dyes is rather to enhance colour sensitiveness than to create it. It is very extraordinary that some types of dyes are far more energetic in their sensitizing powers than others. Thus the fluorescein derivatives are particularly vigorous, the cyanin and isocyanin derivatives similarly. Some dyes—such as, for example, benzo green—are almost inactive with silver gelatino-bromide plates, whilst with collodion emulsion

they enhance enormously the colour sensitiveness to some spectral region.

Just as fluorescent dyes transfer a portion of the light they absorb into light of longer wave-length—*e.g.*, quinine, fluorescein, etc.—so colour-sensitizing dyes enhance the sensitiveness of silver bromide to rays of longer wave-length than those they absorb. But the difference between the positions of the absorption and sensitizing bands is in no wise fixed—though it appears to be comparable, from experiments carried out by the writer, with dyes of similar constitution—and there also appears to be some similarity in the distance between the positions of the transmission bands and sensitizing bands. The following are the approximate positions of the absorption and sensitizing bands of some dyes, and the differences between them :

Dye.	Absorption Band.	Sensitizing Band.	Difference.
Benzo green	5950	6600	650
Diazo black BHN	5720	6700	980
Erythrosin	5180	5400	220

Theories have been put forward that the band of sensitiveness due to a dye is generally a short distance to the red side of the absorption band of that dye—thirty Ångström units, for example. It will be seen from the above table that such cannot be the case. That the distance between absorption and sensitizing bands may be equal, or similar, with dyes of similar constitution is perhaps possible, as already suggested.

It may be assumed that in all cases where a dye enhances colour sensitiveness it does so because it has formed a complex dye salt with a portion of the silver haloid in the sensitive film, which salt absorbs light of certain wave-lengths and transforms the light energy into chemical energy, or

‘photo-energy.’ The complex salt is most probably different in colour from the dye itself, and hence the shift in the position of the colour-sensitizing maximum from that of the absorption band.

The action of silver nitrate on the dye is very remarkable in some instances, whilst ammonia in almost all cases increases its action. The mere bathing of a fairly rapid plate in ammonia and drying it imparts to it greater red sensitiveness, as does also a short exposure to light\* and subsequent bathing with ammonia; such plates have been used for work up to  $\lambda = 8200$  A.U. A solution of erythrosin will sensitize for the yellow-green region much more powerfully if it be made alkaline with ammonia, and if, further, some silver nitrate be employed the action will be yet more vigorous. The solution which has given the most powerful sensitiveness to the yellow-green region is, according to *Pizzighelli*, as follows:

A. Erythrosin, 1 : 1000 aqueous solution.

B. Silver nitrate, 1 : 1000 aqueous solution.

Mix 100 c.c. A	} Silver ‘erythrosinate’ is thus formed, and is re- dissolved by the excess of ammonia.
100 c.c. B	
200 c.c. distilled water	
4 c.c. ammonia	

The conclusions arrived at by the writer from an exhaustive series of experiments are:

1. That any anilin dye is capable of enhancing the sensitiveness of silver bromide to some portion of the spectrum.
2. That practically all anilin dyes whose ammoniacal solutions are very little active show distinctly greater action when used in conjunction with silver nitrate, a silver salt of the dye, soluble in excess of ammonia, probably being formed.
3. That dyes whose solutions fluoresce, or show several

\* *Lehmann, Archiv für Wissenschaftliche Photographie*, 1900, ii. 216.

absorption bands, are in general more active than those whose solutions are not complex, and that dyes confer as many maxima of colour sensitiveness as they possess absorption bands.

4. That metallic electrolytes other than solutions of silver salts do not influence the sensitizing action of the dyes, except where they act as mordants or otherwise alter their absorption spectra.

*Eder*\* concludes that any dye which gives striking colour sensitiveness must colour the silver haloid grains, and this has been substantiated by Kieser and others.

However well a plate may be colour sensitized, a portion of the ultra-violet rays and the blue-violet rays affect it to a much greater extent than the green, yellow, and red rays, and this is more especially the case with a grating spectrograph, where the blue-violet region is very much less extended than in the case of a prism spectrograph, whilst the red region is much more extended.

In order to depress the ultra-violet and blue-violet rays so that an even action is obtained throughout the entire spectrum, it will be found a great advantage to place a glass cell in front of the slit containing a solution of some yellow dye, such as tartrazin, its strength being regulated according to the dictates of experiment. A dye we have found particularly suitable for the purpose is *Ceres yellow I.* (Bayer), and we use an alcoholic solution, of concentration 1 : 240,000, in a glass cell of 10 mm. width.

\* Eder, 'Die Praxis der Photographie.'

## CHAPTER VIII

Absorption bands in inorganic and organic substances—Absorption bands and chemical constitution.

ANY coloured liquid placed between the slit of the spectrum and a source of white light very naturally gives an absorption band in the spectrum, or several absorption bands in the case of many spectra. The bands obviously vary if the solution be concentrated or diluted. In some cases the manner in which a band broadens as the solution is concentrated is sufficient to provide accurate data regarding the chemical constitution of the dissolved substance.

The colour changes produced when to a solution of a coloured salt another substance is added which reacts chemically with it have been carefully studied by Jones\* and others. Knowledge as to the nature of hydrates in aqueous and other solutions will doubtless be forthcoming from the investigations now being carried on into the spectra of dissolved substances. When a substance is dissolved in water, it is at present an unsolved problem, according to Hartley,† what the exact constitution of the resulting liquid is. If the salt be anhydrous, it may possibly combine with the water to form a more complex molecule, which in its turn is dissolved, or the whole of the water may combine with the salt to form a still more complex molecule.

\* 'Hydrates in Aqueous Solutions,' 1907.

† Trans. Roy. Dub. Soc., 1900, 254.

From Vaillant's\* studies of electrolytes in solution, it appears that the ions possess their own colours independently of the molecules, and that the addition of an electrolyte quite colourless in itself is capable of modifying the colour of a solution containing another electrolyte with a coloured ion, either by changing the dissociation or by causing dehydration. The two actions have no connexion, and, as would seem probable, the dehydration would be due to the tendency of the added electrolyte to form hydrates.

As examples, cobalt nitrate in aqueous solution exists as the hexahydrate,  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ . It is possible to add to the solution another nitrate which causes an altered degree of dissociation, which is accompanied by an alteration in the absorption spectrum. Cobalt chloride similarly exists in aqueous solution as  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ , but if the concentration be made sufficiently great, it gives place to the double hydrate  $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ , which has a totally different absorption spectrum.

When a large percentage of soluble chloride is added to dilute cupric chloride solution the colour changes, and the absorption band consequently alters.

If a solution of potassium permanganate be examined, it will be found to possess one wide absorption band when the concentration is sufficiently great, whilst as the concentration diminishes several absorption bands gradually make their appearance; if, now, to the solution a few drops of a weak solution of a soluble thiosulphate be added, the permanganate will become decomposed and the bands will disappear, because the reduction products of the action are insoluble, and cannot, therefore, colour the solution.

Professor Hartley has done a vast amount of work in connexion with absorption spectra, and in a communication

\* *Ann. Chim. Phys.*, 1903, vii. 28.

to the Royal Dublin Society in 1900 many details of interest are to be found.

The spectra of metallic salt solutions are divided by him into three classes:

1. Continuous spectra.
2. Groups of rays of different refrangibilities separated by one or more absorption bands.
3. Spectra interrupted by sharp black bands or lines.

The second group includes solutions of such substances as blood, chlorophyll, fuchsin, and so on. The third group includes solutions of uranium salts, and salts of didymium, samarium, erbium, etc. Many such absorption spectra, with full details, are supplied in Hartley's paper.

The effect of heat on the absorptions of various metallic salt solutions was also investigated, and two results are given below:

Salt.	Temp.	Observations.	$\lambda$
Violet chromium sulphate, $\text{Cr}_2(\text{SO}_4)_3 \cdot 15\text{H}_2\text{O}$ , 0.5 gramme in 4 c.c. of water.	16° C.	Spectrum begins at ...	662
		Rays transmitted to ...	562
		Absorption band ...	562/525
		Spectrum ends at ...	423
	100° C.	Spectrum begins at ...	662
		Rays transmitted to ...	577
		Absorption band ...	577/526
Chrome alum, $\text{KCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ .	37° C.	Spectrum begins at ...	685
		Rays transmitted uninterruptedly to ...	470
	100° C.	Spectrum begins at ...	685
		Absorption band ...	627/543
		Rays transmitted to ...	503

Some conclusions arrived at from an extended study of absorptions were the following: That absorption spectra of

different salts of the same metal are not identical even when the spectrum is a marked characteristic of the metal; when a saturated solution of a coloured salt undergoes a change of colour on dilution, that the dilution usually gives rise to considerable heat; that heat usually causes a widening of the absorption bands or a slight intensity of the absorption.

In Fig. 57 are seen spectrograms of a continuous spectrum, with a cell 10 mm. wide intercepted between the slit and the

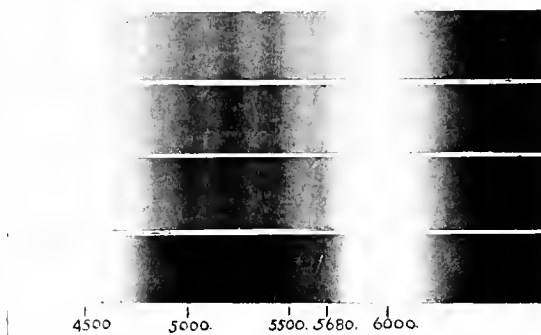


FIG. 57.

light source, with various concentrations of potassium permanganate.

A wedge-shaped cell is especially useful for this kind of work, and no measurements have much practical value unless the width of the cell and the concentration, temperature, etc., of the solution be noted.

The most practical applications of the spectral measurement of absorptions are those made to organic chemicals, when the constitution of a compound can be determined by drawing a curve showing the *variations* in the absorption band or bands with alterations in the concentrations. Very numerous practical examples and measurements will be found in Kayser's 'Handbüch der Spectroscopie'; but, as an explanatory example, we will take a curve given in 1882 by



Hartley, in a paper communicated to the Chemical Society on the constitution of certain organic compounds. He used the cadmium lines as a means of mapping out the absorptions, and the shape of the curve by photographing the spectrum through solutions, of varying concentrations, of  $\alpha$ -pyridine-dicarboxylic acid, is seen in Fig. 58.

If a coloured compound is not a salt, its colour may be said to be *constitutive*, whilst a salt at infinite dilution can be

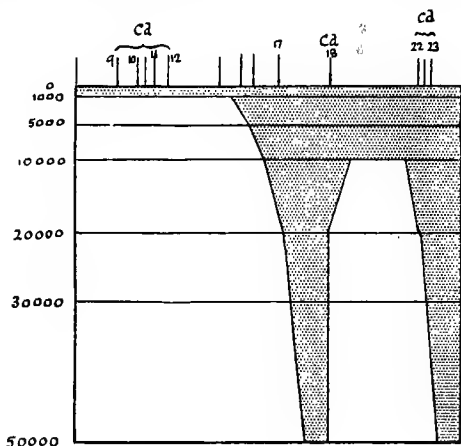


FIG. 58.

dissociated into its ions, and its absorption spectrum is due to the sum of the ions' absorptions.

It is the constitutive colours, or absorptions, which enable us to differentiate between organic compounds.

Baly has recently done much work in connexion with this branch of spectroscopy, and he uses the iron arc, which contains about 1,000 lines, as the source of illumination, measuring off the absorption bands of the substance with solutions of different concentrations, or different thickness of one concentration of the solution in question. Amongst the fatty compounds the spectra are practically all con-

tinuous, whilst many of the aromatic compounds give one or more absorption bands fairly well defined. It is possible to distinguish between isomerides in many cases, whose absorptions differ according to their constitutions.

The absorption bands of the aromatic compounds are more especially in the ultra-violet; the anilin dyes offer a wide field of research, however, which has as yet been very little trodden. In Fig. 59 is seen a series of spectrograms of the sodium salt of the tetriodide of fluorescein, together with the curve showing the general character of the absorp-



FIG. 59.

tion band, and the variation in shape of the band according to concentration.

Baly has suggested that an absorption band appears wherever there is tautomeric change within the molecule, and his hypothesis has already been applied with success to several cases of keto-enolic tautomerism.

The study of absorption bands is therefore of importance in connexion with physical chemistry for the ascertaining of structural data which have not been definitely established by other means, and for an auxiliary aid to difficult organic analysis; similarity in absorption undoubtedly indicates similarity in the compounds themselves.

Full information on this work will be found in Kayser's

splendid treatise already referred to, whilst some of the most recent papers on the subject will be found in the *Journal of the Chemical Society* for 1906, contributed by Baly, Stewart, and others.

Stark considers that all substances which absorb light fluoresce, and in all probability the shift in the fluorescent band from the absorption band will furnish interesting and reliable details as to the structure of organic compounds. Francesconi and Bargellini found, in examining a great number of substances, that aliphatic compounds are non-fluorescent, and that all aromatic compounds exhibit fluorescence or possess the power to fluoresce under certain conditions.

## CHAPTER IX

Arrangements in the lines in spectra—Balmer's formula for the hydrogen series—Possibility of atomic weight determinations—Zeeman effect.

IF the arc spectrum of iron or vanadium be examined, it will at once appear evident that there is some similarity between certain of the groups of lines present. The frequency of the vibrations, which cause the luminosity of a body under examination, are doubtless intimately connected with the frequency of the vibrations within the molecules of that body, and the further probability thus exists that connexions can be found between the lines given by metals similar in physical and chemical properties.

*Balmer* discovered that wave-lengths of the principal lines in the *hydrogen spectrum* can be calculated from the formula

$$\lambda = 3645 \cdot 6 \left( \frac{m^2}{m^2 - 4} \right),$$

where  $m$  is any whole number between 3 and 11. Or if  $\nu$  be the oscillation frequency—i.e.,  $1/\lambda$ —we have

$$\nu = 27418 \cdot 7 (1 - 4m^{-2}).$$

It is clear that, as  $m$  becomes greater, the value of  $\nu$  becomes more and more nearly equal to 27418·7; this constant is termed the *convergence frequency*.

As a rule, one expression is not applicable to the whole of the lines in a spectrum, and three series are frequently found,

the principal, the first subordinate, and the second subordinate series. Thus *Kayser and Runge* have found formulæ connecting three such series in the case of potassium, sodium, lithium, etc., in some cases where pairs of lines are met with instead of single lines two very nearly equal formulæ being necessary. The formulæ of Balmer and Kayser and Runge are of the form

$$o = K \left( 1 - \frac{x}{K} m^{-2} - \frac{y}{K} m^{-4} \right);$$

thus if  $y=0$ , and  $K=27418.7$ , we get the formula already given for the principal hydrogen lines. Similarly, the formula for the principal sodium series is given as

$$o = 41536.8 \left( 1 - 3.12939 m^{-2} - 19.33950 m^{-4} \right).$$

The subject of series of lines in spectra is fully dealt with in other text-books, and we shall only, therefore, deal here with one of the points in connexion with it which has a direct bearing on chemical work.

It will be, perhaps, suitable to quote from an abstract of a communication by Dr. Marshall Watts,\* which appeared a short time ago in the *Journal of the Chemical Society*: 'Two distinct kinds of *connexion between the spectra* of allied elements appear to exist. In the first, the differences between the oscillation frequencies of certain lines of one element are to the differences between the frequencies of the corresponding lines of the second element in the same ratio as the squares of their atomic weights. This is the case in the zinc, cadmium, and mercury family. In the second class, the element of greater atomic weight has the smaller frequency, and if a corresponding line in the spectrum of three elements be compared, the differences of frequency are proportional to the differences between the squares of the atomic weights.

\* *Phil. Mag.*, 1903, 6, 5.

‘In the first case, the atomic weight of one element can be calculated from that of the other element; in the second case, from those of the two other elements, if the correspondence of the lines be assumed. Thus, from the frequencies of twenty-four lines in the spectra of zinc and cadmium, values ranging from 64·69 to 65·69 are obtained for the atomic weight of zinc. In the second class, values from 87·2 to 87·8 are obtained for the atomic weight of strontium, those of barium and calcium being known.’

*Ramsey*\* has done some interesting work in connexion with potassium, rubidium, and cæsium, and their mutual relations. The lines were divided into principal and *first and second subordinate series*. Diagrams were made in which the oscillation frequencies are abscissæ, and the atomic masses, or their squares, are ordinates; these show the close connexion between the spectra and the atomic masses.

If squares of atomic weights be plotted against oscillation frequencies, the lines joining up corresponding points are nearly straight in certain ascertained cases, and if several such lines be obtained they themselves are often almost parallel.

As an actual example, let us assume that the lines given below correspond to one another in the case of the three elements *calcium*, *strontium*, and *barium*.

Metal.	Oscillation Frequency of Corresponding Lines.	
	I.	II.
Calcium -	15387	17873
Strontium	19388	22061
Barium	21617	24390

Now refer to Fig. 60. Here we have oscillation frequencies as ordinates and squares of atomic weights as abscissæ. If

\* Proc. Royal Society, 1902, 70.

we mark on the squared paper the positions of the points obtained by means of Column I., the squares of the atomic weights of calcium, strontium, and barium being taken as  $(40)^2$ ,  $(87.6)^2$ , and  $(137.4)^2$ , we get—by joining the three points—the line AB. Similarly, from Column II. we get the line CD. It will be seen that CD is almost parallel to AB.

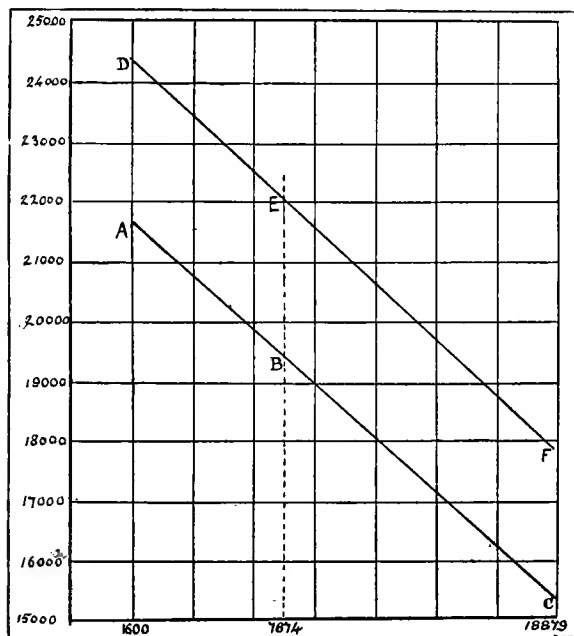


FIG. 60.

Now suppose that in three spectra, two of which were known to be those of calcium and barium, certain corresponding lines were observed and their oscillation frequencies  $\sigma$ , or  $\frac{1}{\lambda}$ , ascertained; by finding two points on the squared paper corresponding to  $(A_C^2, \sigma_C)$  and  $(A_B^2, \sigma_B)$ , where  $A_C$ ,  $A_B$  are the atomic weights of calcium and barium, and  $\sigma_C$ ,  $\sigma_B$  the

oscillation frequencies of the corresponding lines in the spectra of these metals, we could, by finding the abscissa for the point whose ordinate was  $o_8$ , ascertain the *atomic weight* of the metal strontium.

An interesting fact in connexion with the component lines of *doublets* and *triplets* in a spectrum, due to *Hartley*, is that the differences between  $o_1$  and  $o_2$ , and  $o_2$  and  $o_3$ , where  $o_1, o_2, o_3$  are the oscillation frequencies of the components, are the same for all the doublets or triplets in that spectrum.

#### ELECTRO-MAGNETIC CONSIDERATIONS AND THE ZEEMAN EFFECT.

Magnetism is known to have various effects upon light. According to *Maxwell*, the velocity of electrical waves is given by the expression

$$v = \sqrt{\frac{K}{\rho}},$$

where  $K$  is the elasticity and  $\rho$  the density of the medium through which the wave travels; or if we consider  $K$  as the specific inductive capacity of air, and  $\rho$  the permeability, and  $K_m, \rho_m$  these constants for another medium  $m$ , we have

$$v : v_m = \sqrt{\frac{K}{\rho}} : \sqrt{\frac{K_m}{\rho_m}};$$

putting  $\rho = 1$ , in consideration of air and the medium  $m$  having a permeability of nearly 1, we get

$$v : v_m = \sqrt{K} : \sqrt{K_m},$$

but  $\frac{v_m}{v}$  measures the refractive index from air into the medium (Chapter I.); hence if we put  $\frac{K_m}{K} = k$ —i.e., the



*specific inductive capacity* of the medium relative to air—we get

$$\mu = \sqrt{k},$$

or the refractive index equals the square-root of  $k$ , the specific inductive capacity. This is approximately true in the case of certain dielectrics, such as petroleum, benzene, and toluene.

Zeeman found that the yellow sodium lines become widened if the light source be placed between the poles of a powerful electro-magnet. A spectroscope of great dispersive power reveals the fact that the lines become separated into further components.

If examined parallel to the lines of force, a line is seen to split into two, each component being circularly polarized in opposite directions. Examined at right angles to the lines of force, the line is seen to divide into three, the central component being polarized in an equatorial plane, the two side components in a plane passing through the lines of force.

Light is caused by the vibration of electrons, and their vibration periods will naturally be affected by a magnetic field; some motions will be retarded and others accelerated, and hence the splitting up of one line into more will take place.

One important feature of the subject is that similarity evidently exists between the amount of separation, in a given magnetic field, in the lines which form a series, and that some connexion exists between the behaviour of the lines of any two or more series which correspond to each other.

TABLE I.—THE PRINCIPAL FRAUNHÖFER LINES.

Line.	Element due to	Wave-Length.	Oscillation Frequency ( <i>Vacuo</i> ).
A	O	7594·0	13164·6
B	O	6867·5	14557·5
C	H	6563·0	15232·7
D <sub>1</sub>	Na	5896·2	16955·6
D <sub>2</sub>	Na	5890·2	16972·8
D <sub>3</sub>	H	5876·0	17013·8
E	—	5270·1	18969·8
b <sub>1</sub>	Mg	5183·8	19285·6
b <sub>2</sub>	Mg	5172·9	19326·3
F	H	4861·5	20564·1
G	Fe	4308·0	23205·9
H	Ca	3968·6	25190·6
K	Ca	3933·8	25413·4

TABLE II.—THE PRINCIPAL VISIBLE HYDROGEN LINES.

Line.	Wave-Length.
C	6563·0
F	4861·5
γ	4340·7
δ	4101·8
ε	3970·2

TABLE III.—SOME OF THE PRINCIPAL MERCURY LINES (VACUUM TUBE).

Region.	Wave-Length.
Yellow.	5804·3
"	5769·6
"	5679·0
Green.	5461·0
"	5426·5
Blue-violet.	4358·6
"	4347·7

LIQUID SAFE-LIGHTS FOR THE DEVELOPMENT OF  
COLOUR-SENSITIVE PLATES.

It has been thought advisable to give formulæ for preparing green and red safe-lights for dark-room lamp illumination when working with colour-sensitive plates.

1. Green safe-light, for highly red sensitive plates which have minimum sensitiveness in the green—*e.g.*, pinacyanol bathed, benzo-green, and collodion, etc. The glass tank which is fitted into the front of the dark-room lamp is filled with a solution of—Aurantia, 10 grammes; methylene blue, 2 grammes; water, a sufficient quantity to absorb all but a band of the spectrum limited by about  $\lambda = 5500$ – $5600$  and  $\lambda = 5800$ .

2. Red safe-light, for panchromatic or orthochromatic plates sensitive to about  $\lambda = 6500$ : New patent blue; crocein scarlet; naphthol yellow; water, a sufficient quantity to absorb all but a red band beginning at about  $\lambda = 6500$ .

## SILVERING GLASS PRISMS, MIRRORS, ETC.

Dissolve 1 gramme silver nitrate in 250 c.c. distilled water, then add sufficient strong ammonia to very nearly dissolve the brown precipitate at first formed, and dilute with distilled water to make up 100 c.c.; finally, filter it. To a flask containing 0.2 gramme silver nitrate in 100 c.c. boiling distilled water add 0.17 gramme sodium-potassium tartrate, and boil the solution until it becomes grey, then at once filter and allow to cool. Mix the two solutions, and immerse the prism face or glass for an hour or longer, having first thoroughly cleaned it with strong  $\text{HNO}_3$ , strong KOH solution, and rectified spirit, rinsing with plenty of distilled water between each treatment.

## BLACKENING COPPER OR BRASS TUBES, FLANGES, ETC.

Make up two solutions, one containing a gramme of silver nitrate in 100 c.c. distilled water, the other containing a gramme of cupric nitrate in 100 c.c. distilled water. Mix the two solutions, and apply with a wad of cotton-wool to the metal, which must be well polished with emery; whilst wet, hold it in a Bunsen flame, when it will become dull black.

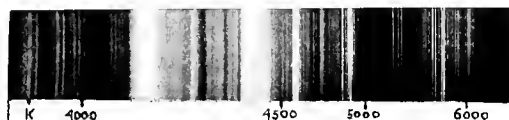


FIG. 61.—SPECTROGRAM SHOWING VANADIUM LINES.

FIG. 62.—SPECTROGRAM OF PURE ARC SHOWING  
BANDS DUE TO N, CO, ETC.FIG. 63.—SPECTROGRAM OF BRASS ARC SHOWING ZN LINES<sup>1</sup>  
IN COPPER.

TABLE IV.—NATURAL SINES OF ANGLES BETWEEN 12° AND 26°, FOR USE WITH PLANE GRATING REPLICAS PLACED NORMALLY TO COLLIMATOR AXIS.

	0'	3'	6'	9'	12'	15'	18'	21'	24'	27'	30'	33'	36'	39'	42'	45'	48'	51'	54'	57'
12°	2079	2088	2096	2105	2113	2122	2130	2139	2147	2156	2164	2173	2181	2190	2198	2206	2215	2223	2232	2241
13°	2250	2259	2267	2276	2284	2293	2301	2310	2318	2326	2334	2343	2351	2360	2368	2377	2386	2394	2402	2410
14°	2419	2428	2436	2445	2453	2461	2470	2479	2487	2496	2504	2512	2521	2530	2538	2547	2555	2563	2571	2580
15°	2588	2597	2605	2614	2622	2630	2639	2648	2656	2665	2673	2680	2689	2698	2706	2715	2723	2730	2740	2748
16°	2756	2765	2773	2781	2790	2799	2807	2816	2824	2831	2840	2849	2857	2865	2874	2882	2890	2899	2907	2915
17°	2924	2932	2940	2948	2957	2965	2974	2982	2990	2999	3007	3016	3024	3032	3040	3048	3057	3066	3075	3083
18°	3090	3098	3106	3115	3123	3131	3140	3148	3156	3165	3173	3180	3190	3198	3206	3215	3223	3231	3239	3248
19°	3256	3264	3272	3280	3289	3298	3306	3314	3322	3330	3338	3346	3355	3364	3372	3380	3388	3396	3404	3413
20°	3420	3428	3436	3443	3452	3460	3469	3478	3486	3494	3502	3510	3518	3527	3535	3543	3551	3559	3567	3575
21°	3584	3592	3600	3608	3616	3624	3632	3641	3649	3657	3665	3673	3681	3689	3697	3706	3715	3722	3730	3738
22°	3746	3754	3762	3770	3778	3786	3794	3802	3810	3818	3826	3834	3843	3851	3859	3867	3875	3883	3891	3899
23°	3907	3915	3923	3931	3939	3947	3955	3963	3971	3979	3987	3995	4003	4011	4019	4027	4035	4043	4051	4059
24°	4067	4075	4083	4091	4099	4107	4115	4123	4131	4139	4147	4155	4163	4171	4179	4187	4195	4202	4210	4218
25°	4226	4234	4242	4250	4258	4266	4274	4282	4290	4297	4305	4313	4321	4329	4337	4345	4353	4360	4368	4376
26°	4384	4392	4399	4407	4415	4423	4431	4438	4446	4454	4462	4470	4478	4485	4493	4501	4509	4517	4524	4532

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